

# Gate Opening, Diffusion, and Adsorption of CO<sub>2</sub> and N<sub>2</sub> Mixtures in ZIF-8

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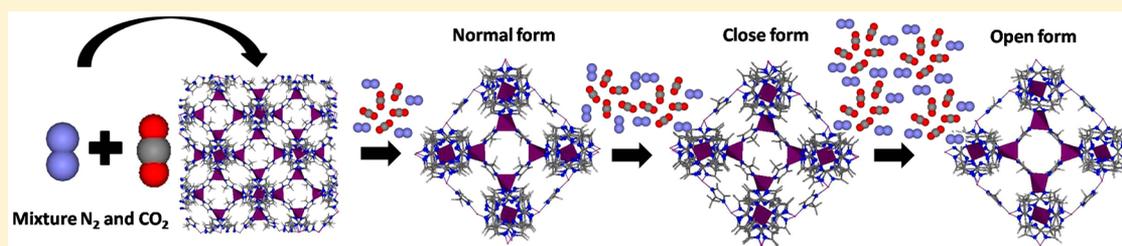
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## S Supporting Information



**ABSTRACT:** Diffusion and adsorption of CO<sub>2</sub>/N<sub>2</sub> mixtures in the zeolitic imidazolate framework ZIF-8 are investigated by molecular dynamics (MD) and Gibbs ensemble Monte Carlo (GEMC) simulations. Structural changes called “gate opening” could be found for the adsorbed single-component gases and for the mixture. The gate opening appears for the mixture at a total number of guest molecules per cavity between that for the pure CO<sub>2</sub> and that for the pure N<sub>2</sub> but closer to that of N<sub>2</sub> which is lower. Due to the stronger dependence of CO<sub>2</sub> adsorption upon the temperature in comparison with N<sub>2</sub>, the adsorption selectivity is predicted to be higher at lower temperatures, which is in accordance with experimental findings.

## 1. INTRODUCTION

Porous materials play an increasing role in research and industry. Particularly, during the past decade metal–organic frameworks (MOFs, see refs 1 and 2) came into the focus of interest because of their great diversity, the big pores, and the possibility of custom-made design. Some of them have the highest internal surface areas per gram of all porous materials known to date (see Li et al.<sup>2</sup>). They consist of metal ions or metal oxide clusters that are connected by organic linkers forming porous frameworks. Replacing the organic linkers, new structures can be created and also exchange of the metal ions or metal ion clusters can change the properties of MOFs thus giving the possibility of tailoring the MOFs to specific applications. For example, Kwon et al.<sup>3</sup> and Krokidas et al.,<sup>4</sup> respectively, could show that replacement of Zn<sup>2+</sup> with Co<sup>2+</sup> in ZIF-8 (resulting in ZIF-67 framework) enhanced significantly the propylene/propane separation.

But, for technical applications, also a high stability against thermal and chemical conditions of use and against pressure changes is required. With respect to the stability a subgroup of the MOFs, the zeolitic imidazolate frameworks (ZIFs), are very promising. Many of them have high thermal and chemical stability (see Park et al.<sup>5</sup>) that makes them interesting materials for potential industrial purposes.

Besides experiments, simulations are important tools for the exploration of such materials. Simulations are safe, comparatively cheap and well-suited to understand or forecast properties of guest molecules in MOFs. They are able to vary conditions to identify reasons for effects. Examples are simulations with rigid and flexible MOF lattice for comparison.

An interesting feature of many MOFs, that is also important for applications, is the lattice flexibility that is much larger than that of other porous materials, e.g., zeolites.<sup>6–11</sup> As an example, in refs 6 and 7 it could be shown that this can result in opening of bottlenecks in the lattice of the MOF Zn(tbip) at high guest molecule concentrations resulting in interesting patterns of the dependence of the self-diffusion coefficient upon the guest molecule concentration. But, even under ambient conditions, the fluctuating size of the so-called windows, that connect adjacent cavities, can have drastic consequences. In Hertäg et al.<sup>6</sup> it turned out that the diffusion selectivity for a CH<sub>4</sub>/H<sub>2</sub> mixture in ZIF-8 was changed by several orders of magnitude due to this effect. The lattice of ZIF-8 is quite flexible so that molecules slightly larger than the average window (bottleneck)

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diameter (3.4 Å from Rietveld refinement) can diffuse due to the window “breathing”.<sup>9,10</sup> This concept could be reproduced only in flexible lattice simulations with appropriate parameters like, e.g., those from the Amber force field<sup>12</sup> or by Haldoupis et al. in *ab initio* molecular dynamics (MD),<sup>10</sup> while parameters from the also well-established Dreiding force field<sup>13</sup> yield a too stiff lattice (see Hertäg et al.<sup>9</sup>). Hence, the choice of appropriate interaction parameters is very important, and not easy. Additionally, the correct simulation of the lattice vibrations requires the definition of about 10 000 elastic bonds, angles, and dihedral angles for an MD simulation box. The consequence is a big programming effort and requirement of computer time. Therefore, simulations in the rigid lattice may appear to be attractive, but this can lead to a diffusion behavior which is far from the experimental findings as shown, e.g., by Hertäg et al.<sup>9</sup>

Moreover, the lattice flexibility can lead to such surprising effects as found by the group of Kapteijn for ethane/ethylene adsorption in ZIF-7 (see refs 14 and 15). It consists in a change of the lattice shape of ZIF-7 that opens bottlenecks and enables larger molecules such as ethane to enter the ZIF-7 structure more easily. The effect was named “gate opening”. By density functional theory (DFT) calculations it could be shown by van den Bergh et al.<sup>15</sup> for this system and by Zheng et al.<sup>16</sup> for ethane in ZIF-8 that this gate opening is, in some cases, based on quantum effects. Hence, it could not be reproduced in classical MD simulations, even not with flexible lattice, for ethane in ZIF-8 (see Chokbunpiam et al.<sup>17</sup>)

ZIF-8 is a well-known member of the ZIFs. In ZIF-8, Zn<sup>2+</sup> ions are interconnected by methylimidazolium anions (mim<sup>-</sup>) forming an SOD lattice of the composition Zn<sup>2+</sup>(mim<sup>-</sup>)<sub>2</sub>. Many experimental and computational studies of ZIF-8 have been published already, e.g., refs 9, 11, 16–35.

Moggach et al. described in ref 26 a structure of ZIF-8 that has been observed at 1.47 GPa under loadings of up to 41 methanol molecules per unit cell. This high-pressure structure shows larger pore volume and larger diameter of the windows that connect adjacent cavities and corresponds to a gate-opening effect. The change is reversible. In order to understand this phenomenon Fairen-Jimenez et al. investigated in ref 27 the high-pressure structure, called ZIF-8HP, by experiment and grand canonical Monte Carlo (GCMC) simulation, and the results are compared with those from the ZIF-8 structure at ambient pressures which is named ZIF-8AP. The authors compared the measured adsorption isotherm of N<sub>2</sub> in ZIF-8 by use of separate GCMC simulations with rigid lattice for the two structures ZIF-8AP and ZIF-8HP and show that at low pressure the simulated isotherm for the ZIF-8AP structure and at high pressure the simulated isotherm for the ZIF-8HP structure agree well with the experiment. It is concluded, therefore, that in reality increasing concentration of N<sub>2</sub> causes a phase transition from ZIF-8AP to ZIF-8HP. The transition itself cannot be simulated with rigid lattice GCMC.

In Zhang et al.,<sup>28</sup> this gate-opening effect was first found in classical MD simulations for N<sub>2</sub> in ZIF-8 at low temperature. This gate opening could also be found by Chokbunpiam et al.<sup>19</sup> at ambient temperature and at a loading that agreed with the experiment. The gate opening was caused by a reorientation of the linker molecules. Other theoretical studies about gate opening that is caused by linker rotation and which can be also called “swinging door motion” or “saloon door motion” include refs 4, 10, and 36. This saloon door motion could also be

examined experimentally by Kolokolov et al.<sup>37</sup> for benzene and by Casco et al.<sup>38</sup> upon N<sub>2</sub>.

Since carbon dioxide is a very important gas in many chemical processes and on the other hand a prominent greenhouse gas, the behavior of CO<sub>2</sub> in ZIF-8 is very interesting with respect to a possible use of ZIF-8 for storage or for separation of CO<sub>2</sub>. Particularly, adsorption at higher pressure is of interest for pressure-swing separations because exposure of the loaded ZIF to ambient pressure is sufficient to release the largest part of the guest molecules and to make the ZIF ready for repeated use. Fairen-Jimenez et al.<sup>29</sup> investigated the adsorption of some gases including CO<sub>2</sub> by experiment and rigid lattice GCMC simulations. For CO<sub>2</sub> at 273 K both structures ZIF-8AP and ZIF-8HP give similar adsorption isotherms for the whole range of pressure (see Figure 4 of this paper,<sup>29</sup> lowest curve on the right). These similar isotherms do not allow drawing conclusions about the existence of gate opening for CO<sub>2</sub>. Therefore, in Chokbunpiam et al.<sup>20</sup> this question has been examined by MD simulations with flexible lattice. It has been shown that a gate opening happens for CO<sub>2</sub> in flexible ZIF-8 at 300 K only for loadings of more than 22 CO<sub>2</sub> molecules per cavity which corresponds to a high pressure which would be above the gas–liquid transition pressure in a connected gas volume. In Venna and Carreon<sup>30</sup> the use of ZIF-8 in a membrane for the separation CO<sub>2</sub>/CH<sub>4</sub> is investigated experimentally. In Zhang et al.<sup>31</sup> it is described how the adsorption of CO<sub>2</sub> in ZIF-8 can be enhanced by a special treatment of the ZIF sample. Experimental adsorption isotherms of CO<sub>2</sub> in ZIF-8 are also shown in refs 21–25, 29, 31–34. All of these papers did also GCMC simulations, and each group found parameters that give agreement with the values of their measurements, respectively. A comparison of some of these quite different isotherms is given by Chokbunpiam et al.<sup>20</sup> In refs 18, 22, and 33 also the diffusion of CO<sub>2</sub> in ZIF-8 is investigated experimentally and by simulations. Experimental values from Chmelik<sup>35</sup> have also been compared with simulation results of Chokbunpiam et al.<sup>20</sup> In ref 11 Zhang et al. examine the adsorption and diffusion of CO<sub>2</sub> in ZIF-8 at high pressure (up to 100 bar) by simulations. The importance of the lattice flexibility for diffusion is demonstrated. Gate opening is not mentioned in ref 11. The diffusion of CO<sub>2</sub> in ZIF-8 is also examined by *ab initio* molecular dynamics (AIMD) calculations by Haldoupis et al.<sup>10</sup>

Nitrogen as the major constituent of air is of high interest for the investigation of mixtures with CO<sub>2</sub>. Several papers report the adsorption of nitrogen in ZIF-8. By Pérez-Pellitero et al.<sup>23</sup> the adsorption properties of CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub> in ZIF-8 at 303 K have been examined. The adsorption of N<sub>2</sub> and of CO<sub>2</sub> in ZIF-8 and modified ZIF-8 are also investigated by Zhang et al.<sup>31</sup> where the single-component adsorption isotherms are found from simulations, while that of the mixture were calculated from single-component data by ideal adsorbed solution theory (IAST), but not from simulations as is done in the present paper. Experimental isotherms for the adsorption of CO<sub>2</sub> and N<sub>2</sub> (single component) for low pressures up to 1 bar are reported by McEwen et al.<sup>21</sup> Like in ref 31 mixture data are predicted in ref 21 by IAST, but not from simulations. The simulations of the adsorption isotherms of Chokbunpiam et al.<sup>20</sup> show excellent agreement for CO<sub>2</sub> with those of McEwen et al.<sup>21</sup>

Battisti et al.<sup>34</sup> investigated the adsorption of several mixtures including CO<sub>2</sub>/N<sub>2</sub> in different ZIFs including ZIF-8 by GCMC and MD at 298 K. For the GCMC simulations the lattice was

**Table 1. Values of the Adsorption Constant  $K$  at 298 K from Gibbon Compared with Values Computed from Published Data of Other Papers<sup>a</sup>**

	this work	McEwen et al. <sup>b</sup>	Simmons et al. <sup>c</sup>	Zhang et al. <sup>d</sup>	Pérez-Pellitero et al. <sup>e</sup>	Liu et al. <sup>f</sup>	Pusch et al. <sup>g</sup>
N <sub>2</sub> , pure	0.26	0.14	0.30	0.15	0.11		
N <sub>2</sub> in mix	0.25	0.14		0.14			
CO <sub>2</sub> , pure	1.06	1.05		0.61		0.62	0.94
CO <sub>2</sub> in mix	0.99	1.05		0.61			

<sup>a</sup>The values for  $K$  are given in molecules per cage and per bar. <sup>b</sup>Ref 21. <sup>c</sup>Ref 24. <sup>d</sup>Ref 31. <sup>e</sup>Ref 23. <sup>f</sup>Ref 32. <sup>g</sup>Ref 33.

assumed to be rigid as in most adsorption simulation studies. The MD simulation was carried out with flexible lattice applying the Dreiding force field. The lattice structure has not been investigated, e.g., with respect to the gate-opening effect. Because the independent variable of state in GCMC is the chemical potential rather than the pressure, an additional relation between the chemical potential and the gas-phase pressure is needed. Battisti et al.<sup>34</sup> used the van der Waals equation of state for this purpose. The van der Waals equation is known to be less accurate than, e.g., the Peng–Robinson equation. This may lead to some inaccuracy in the adsorption results. For the membrane selectivity or permeation selectivity of CO<sub>2</sub>/N<sub>2</sub> in the low-pressure limit a value of 5.72 is reported by Battisti et al.<sup>34</sup> Structural details like radial distribution functions or adsorption sites have not been investigated in ref 34.

In the present paper the adsorption and diffusion of CO<sub>2</sub>/N<sub>2</sub> mixtures in ZIF-8 are examined by both MD with flexible lattice and Gibbs ensemble Monte Carlo (GEMC) with rigid lattice. In MD, dynamical properties of the adsorbed molecules in mixtures and their influence on the flexible lattice are investigated, which was not done in refs 31 and 34. Particularly, the question whether the classical MD simulations will give a gate-opening effect also for this system is examined.

The influence of the temperature on the adsorptive CO<sub>2</sub>/N<sub>2</sub> separation is investigated. This adsorptive CO<sub>2</sub>/N<sub>2</sub> separation is of special interest in the so-called “post combustion” strategy to extract CO<sub>2</sub> from power plant exhaust gases after steam has been removed by condensation.

The self-diffusion coefficients of CO<sub>2</sub> and N<sub>2</sub> are evaluated so that the diffusion selectivity can be calculated. From the adsorption and diffusion selectivities the membrane selectivity can be obtained.

## 2. COMPUTATIONAL DETAILS

**2.1. Interaction Parameters.** For the lattice atoms of the MOF and for CO<sub>2</sub>, the interaction parameters are the same as in Chokbunpium et al.<sup>20</sup> They showed good agreement of the simulated self-diffusion coefficient of CO<sub>2</sub> in ZIF-8 with experiments, and also the adsorption isotherms were found to be within the range of various experimental isotherms. Best agreement was found with the isotherm of McEwen et al.<sup>21</sup> For N<sub>2</sub> in ZIF-8, the same parameters as in Chokbunpium et al.<sup>19</sup> are used. In ref 19 the structural phase transition in ZIF-8 has been investigated, but not the adsorption of guest molecules.

To check the interaction parameters, tests at low pressure are carried out. In order to include also the results of McEwen et al.<sup>21</sup> (where the adsorption has been investigated only at low pressure) in our comparison, we used the linear low-pressure part of the adsorption isotherm to check the consistency of our parameters by experimental adsorption results.

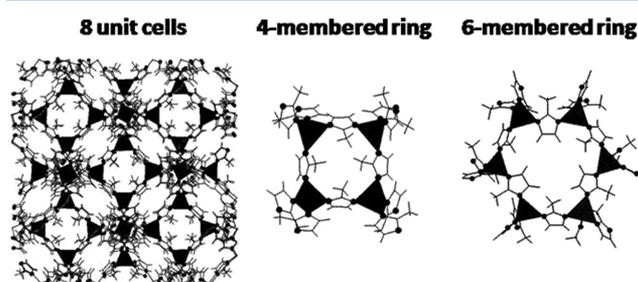
As the uptake  $u$  of N<sub>2</sub> and CO<sub>2</sub> in ZIF-8 at 298 K follows at low pressures  $p$  a linear law (analogous to Henry's law)

$$u = Kp \quad (1)$$

it might be interesting to compare for pressures up to 5 bar the adsorption constant  $K$  from different papers with  $K$  values obtained in the present paper by simulation. Note that the concept of the Henry law comes from dissolution of gases in liquids, and in such applications, the Henry constant is usually defined in a way that is slightly different from our  $K$ .

The validation of the used parameters by comparing values of  $K$  of this paper with those obtained from published adsorption isotherms is presented in Table 1 and discussed in the Results and Discussion, section 3.6.

**2.2. Molecular Dynamics Simulations.** The zeolitic imidazolate framework-8 (ZIF-8) structure, has been derived from X-ray diffraction (XRD) data by Park et al.<sup>5</sup> The Mercury program has been used to construct a lattice containing eight unit cells as shown in Figure 1.

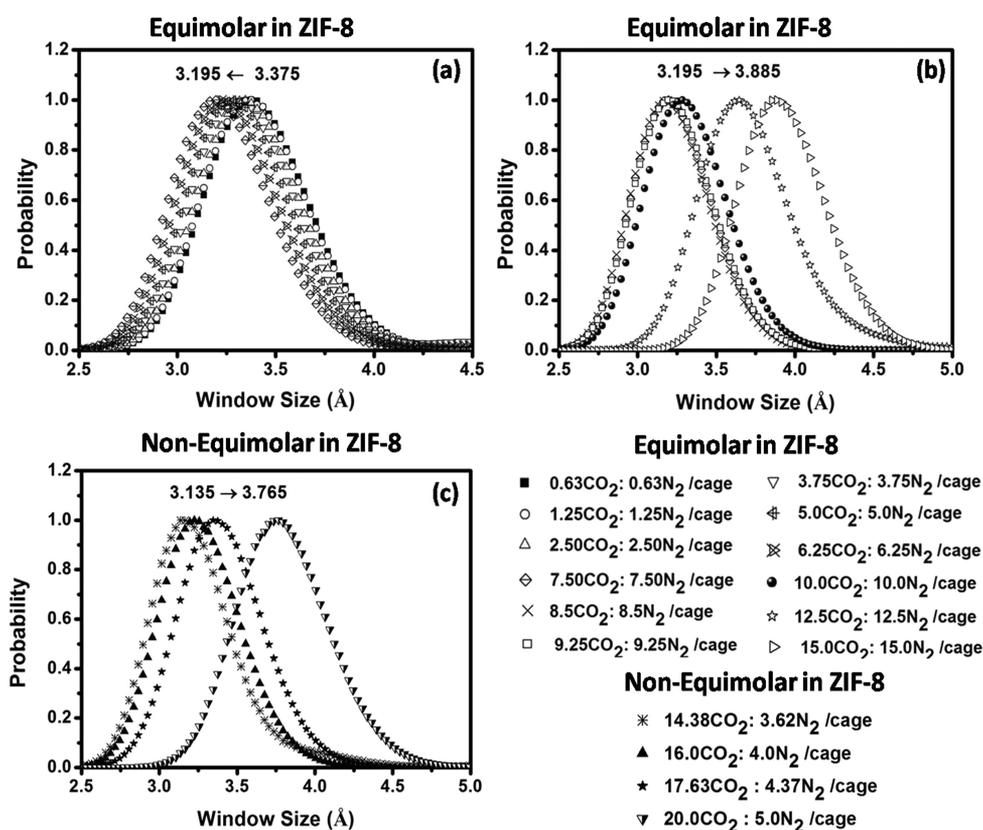


**Figure 1.** ZIF-8 structure consisting of zinc (Zn<sup>2+</sup>, tetrahedra) which is connected by imidazolate linkers that consist of nitrogen (N, circle), carbon (C, line), and hydrogen (H, line).

These eight unit cells of the ZIF-8 form the cubic simulation box (edge length 33.982 Å) for the MD simulations by the DL\_POLY software. We used flexible models for ZIF-8 like in earlier papers of Chokbunpium et al.<sup>17,20</sup> The parameter data for N<sub>2</sub> and CO<sub>2</sub> were taken from Potoff et al.<sup>39</sup> and Liu et al.<sup>32</sup> First, simulation in the isochoric–isothermal ensemble (NVT) is carried out to equilibrate the system for 5 ns. Then, the evaluation part of the run of 25 ns is done in the microcanonical ensemble (NVE) with an average temperature of 298 K which is close enough to 300 K. The integration time step is 2 fs, the VDW interaction cutoff was 14 Å, and Ewald summation was done. The stability of the lattice for our parameters without fixed box size was tested by NPT simulations of the empty lattice at 1 bar as already reported by Chokbunpium et al.<sup>17</sup>

The window size fluctuations and the diffusion coefficients of N<sub>2</sub> and CO<sub>2</sub> as mixture in ZIF-8 are investigated. Finally, we compare our simulation results with the experimental data and computer modeling.

**2.3. GEMC.** Gibbs ensemble Monte Carlo simulations (GEMC, see Panagiotopoulos<sup>40</sup>) of the adsorption isotherm



**Figure 2.** Distribution of the window size (six-membered rings) of ZIF-8 for mixtures with different loadings at 300 K. Slight decrease of the window size with increasing loading (a). Large increase of the window size with increasing loading (b and c).

are done using the homemade Gibbon software that has been used successfully by Chokbunpiam et al.<sup>20</sup> for pure CO<sub>2</sub> already. In GEMC, the equilibrium between the gas and adsorbed phases is established by particle exchange between two simulation boxes, box A containing a free bulk gas and box B containing the porous crystal with the adsorbed phases.

GEMC directly yields the equilibrium between the adsorbed phase of the mixture and the gas phase, in which the pressure can be calculated from the density by an equation of state. In GCMC, only the adsorbed phase is included in the simulation and the calculation of the pressure must be done by the virial theorem that is not very accurate for nonspherical, charged particles at high pressure, or alternatively, an additional relation between chemical potential and pressure would be needed.

The adsorption isotherm is normally given in form of uptake as a function of the pressure. GEMC simulations yield the uptake as a function of the density in the connected gas phase. Agreement with the common form of description requires the calculation of the pressure in the gas phase. For low pressures up to about 1 bar, the ideal gas law can be used. To calculate the pressure at higher gas-phase densities, we have used the Peng–Robinson equation of state<sup>42</sup> for both pure substances and also for the mixture. The fact that the density in the gas phase is obtained without any detour that would use, e.g., the chemical potential, which cannot be measured directly, is the main advantage of the GEMC method over GCMC.

A phase transition of gas/liquid happens for pure CO<sub>2</sub> at 298 K at about 64 bar in the free bulk gas. Our Gibbon software is not able to simulate states that include gas/liquid coexistence in the gas-phase box because of the periodical boundary conditions. To be sure to avoid any artifacts like existence of

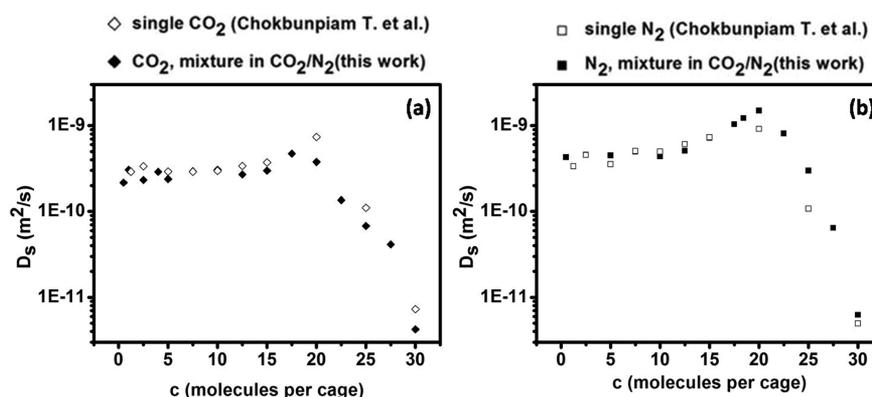
droplets, etc., we did GEMC for pure CO<sub>2</sub> and for the mixture that contains CO<sub>2</sub> only in the pressure range up to 50 bar.

The GEMC simulations are carried out with rigid lattice and rigid molecules because in several papers it has been found already that the adsorption isotherm is much less sensitive against the approximation of a rigid lattice than diffusion<sup>11,41</sup> as long as no structural transitions (e.g., gate opening) happen. Hence, before GEMC with rigid lattice can be done, a structural phase transition for the system and the pressure range that is examined must be excluded. This can be done, e.g., by MD simulations with flexible lattice. In the present paper, GEMC is done only at pressures far below the pressure where gate opening is observed.

One advantage of rigid lattice Monte Carlo (GEMC or GCMC) in comparison to MD with flexible lattice is that the position changes of the molecules per simulation step in the GEMC are about 2 orders of magnitude larger than in MD with flexible lattice, which leads to much better statistics. Moreover, in flexible lattice MD, all the forces connected with elastic bonds, elastic angles, and elastic torsion in the lattice must be calculated in each step. They are very computer time expensive because they include three-body forces and four-body forces. Thus, Monte Carlo with flexible lattice would not be effective and, hence, cannot be found in the literature for adsorption simulations. On the other hand, MD is necessary to investigate time-dependent phenomena, e.g., diffusion, lattice vibration, etc.

We used the same interaction parameters for both the GEMC simulations and the MD simulations in this paper.

In each run the random starting situation is relaxed to equilibrium by an equilibration period of typically 10 million to



**Figure 3.** Molecular self-diffusion of  $\text{CO}_2$  and  $\text{N}_2$  at 300 K for the single-component loadings of 0.5–30 molecules/cage and the mixed gas loadings of 0.5  $\text{CO}_2$ /0.5  $\text{N}_2$  to 15  $\text{CO}_2$ /15  $\text{N}_2$  molecules/cage in ZIF-8 framework by MD simulations.

20 million simulation cycles. Higher densities needed a longer equilibration period. After equilibrium was established, the evaluation takes place during another 10–20 million simulation steps.

For the adsorption isotherms of the mixture at 298 and 273 K we did two kinds of equimolar simulations. In case A we kept the ratio of the numbers of guest molecules of the two molecular species  $\text{CO}_2$  and  $\text{N}_2$  as 1:1 constant in box A (gas box), but changed the gas box size, thus realizing different densities of guest molecules in the gas phase, which means different pressures. Because a change of the box size will normally affect this ratio, the particle numbers were then modified by trials in such a way that the ratio of the two guest molecule numbers was with a remaining difference of about 1% again 1:1 in box A for each case in the equilibrium state. From these equilibrated systems we then calculated the adsorption isotherms and the adsorption selectivity and the fugacities. In case B we modified for each gas volume the ratio of the two guest molecule numbers in box A by trials. After each trial the system had to relax in an equilibrating simulation run. Then the resulting ratio of the particle numbers in box B showed if additional trials and relaxations were necessary to obtain equimolar mixture in box B.

### 3. RESULTS AND DISCUSSION

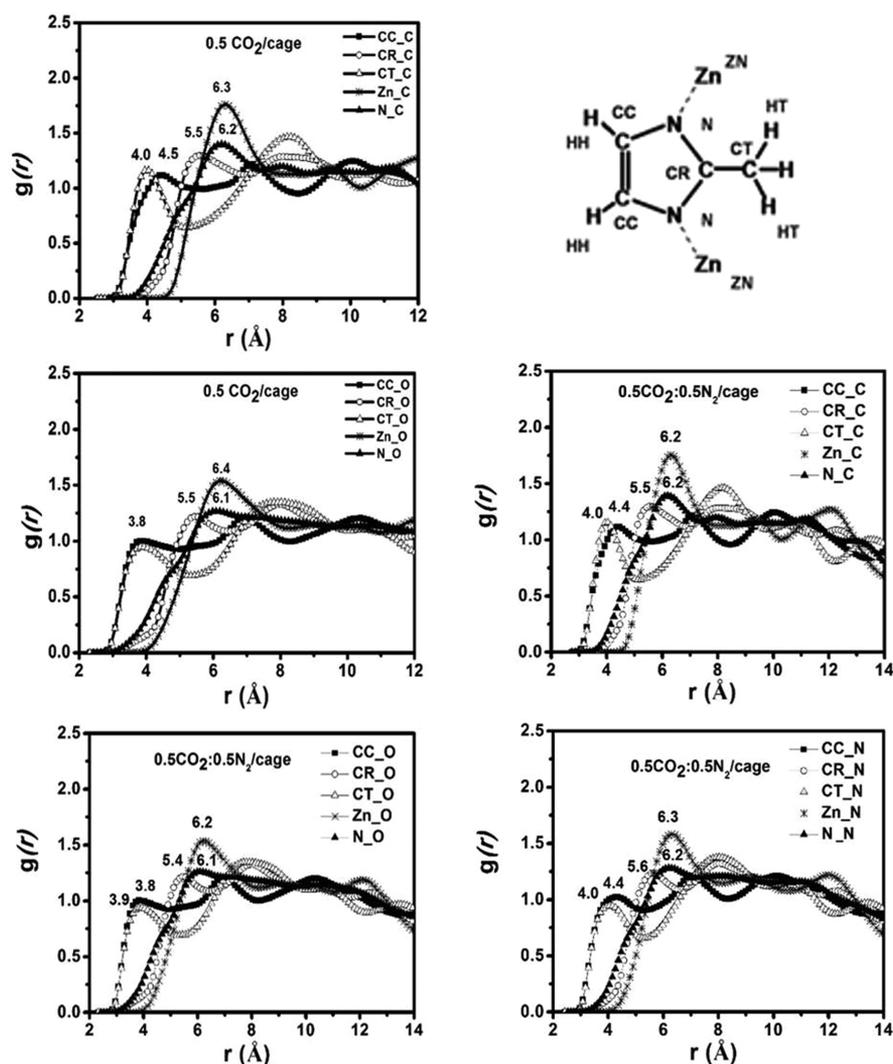
**3.1. Influence of the  $\text{CO}_2/\text{N}_2$  Mixtures in ZIF-8 on the Window Size Found in MD Simulations.** Figure 2 shows the change of the window size with the loading for mixtures of  $\text{CO}_2$  and  $\text{N}_2$ . At low loadings (Figure 2a) the window sizes become slightly smaller from 3.375 to 3.195 Å. However, from 10  $\text{CO}_2$ /10  $\text{N}_2$  to 15  $\text{CO}_2$ /15  $\text{N}_2$  for equimolar adsorbed mixtures in ZIF-8 (Figure 2b) a gate opening up to more than 3.7 Å can be observed. For the adsorbed mixture of the composition  $\text{CO}_2/\text{N}_2 = 4:1$  in ZIF-8 (Figure 2c) the gate opening starts at 16  $\text{CO}_2$ /4  $\text{N}_2$ .

Therefore, the window sizes from single-component gases  $\text{CO}_2$ ,  $\text{N}_2$ , and  $\text{CO}_2/\text{N}_2$  mixture adsorption can be ordered<sup>17,20</sup>  $\text{CO}_2 > \text{CO}_2/\text{N}_2 > \text{N}_2$  (4.125 > 3.885 > 3.585). These results confirm that  $\text{CO}_2$  has a much larger effect on the window size of the ZIF-8 framework than  $\text{N}_2$ .

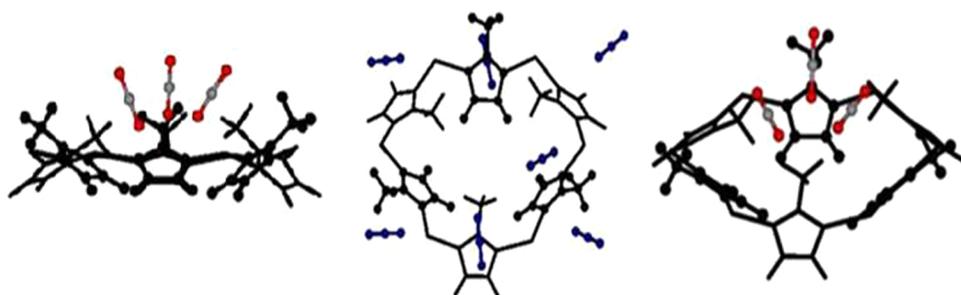
Adsorbed  $\text{N}_2$  and  $\text{CO}_2$  as single-component gases at 298 K were shown by Chokbunpiam et al.<sup>19,20</sup> to lead to the gate opening at loadings of 18.44 and 22.5 molecules/cage, respectively. For the equimolar adsorbed mixture  $\text{CO}_2/\text{N}_2$  in ZIF-8 gate opening was found at 10  $\text{CO}_2$ /10  $\text{N}_2$ , i.e., for 20 guest molecules/cage. Thus, gate opening is found for a mixed

loading which is closer to the transition loading of pure  $\text{N}_2$  than to that of pure  $\text{CO}_2$ . This can probably be explained in terms of the fugacities: a 4 times higher fugacity of  $\text{N}_2$  than that of  $\text{CO}_2$  is necessary to have an equimolar adsorbed mixture  $\text{CO}_2/\text{N}_2$  as shown by GEMC at pressures up to 50 bar (see Figure 10). Assuming that also at higher pressures (not accessible for GEMC) the fugacity of  $\text{N}_2$  is higher than that of  $\text{CO}_2$ , the dominance of  $\text{N}_2$  is plausible. Interestingly, also for the 4:1 ratio  $\text{CO}_2/\text{N}_2$  the gate opening starts at a total loading of about 20 guest molecules/cage. The fugacity of  $\text{N}_2$  for the 1:1 ratio of  $\text{CO}_2/\text{N}_2$  in the gas phase at pressures up to 50 bar is also higher than that of  $\text{CO}_2$ , and the difference increases more than linearly with the loading. But for total loadings of 20 molecules/cage the bulk free mixture outside of the ZIF cannot be examined by our GEMC as mentioned.

**3.2. Diffusion Coefficients of the  $\text{CO}_2/\text{N}_2$  Mixture in ZIF-8.** The self-diffusion coefficients are shown in Figure 3. All self-diffusion coefficients  $D_s$  of  $\text{CO}_2$  and  $\text{N}_2$  as single-component gas as well as in the mixture  $\text{CO}_2/\text{N}_2$  were found to be around  $10^{-9}$  to  $10^{-12}$   $\text{m}^2/\text{s}$  and follow a similar trend. For the single-component gases,  $D_s$  did not change significantly at low loadings, but for loadings above 20.0 molecules/cage, respectively, in refs 19 and 20 the  $D_s$  values of  $\text{N}_2$  and  $\text{CO}_2$  drop dramatically down to  $10^{-12}$   $\text{m}^2/\text{s}$ . The same can be observed for the mixture. These results are interesting in connection with the transition structure and the change of the window size as a function of loading as shown in the above section. Obviously, with increasing loading of gas molecules in ZIF-8, the mutual blocking by molecular collisions has a stronger influence than the gate opening. Interestingly, the radial density functions (RDFs) do not indicate significant changes in the structure of the adsorbed mixture in comparison to single-component  $\text{CO}_2$  adsorption. Such changes could be important for diffusion. From the RDFs reported here (for pure  $\text{CO}_2$  see Figure S3 of the Supporting Information) and those of Chokbunpiam et al.<sup>19</sup> it follows that the maximum height of the first peak for C–C (means carbon atoms of two  $\text{CO}_2$  molecules) is 3.2 in the pure gas simulation and 3.5 in the mixture. For C–O (means carbon atom of one and O atom of another  $\text{CO}_2$  molecule) it is 2.0 in the pure gas simulation and 2.0 in the mixture. For O–O (means oxygen atoms of two  $\text{CO}_2$  molecules) it is also 2.0 in the pure gas simulation and 2.0 in the mixture, and for N–N (means nitrogen atoms of two  $\text{N}_2$  molecules) it is 2.0 in the pure gas simulation and 2.3 in the mixture. Significant differences that would indicate structural changes do not appear.



**Figure 4.** RDFs between atoms of guest molecules with lattice atoms in single-gas  $\text{CO}_2$  and  $\text{CO}_2$  and  $\text{N}_2$  in the mixture  $0.5 \text{CO}_2/0.5 \text{N}_2$  in ZIF-8 at low loading.



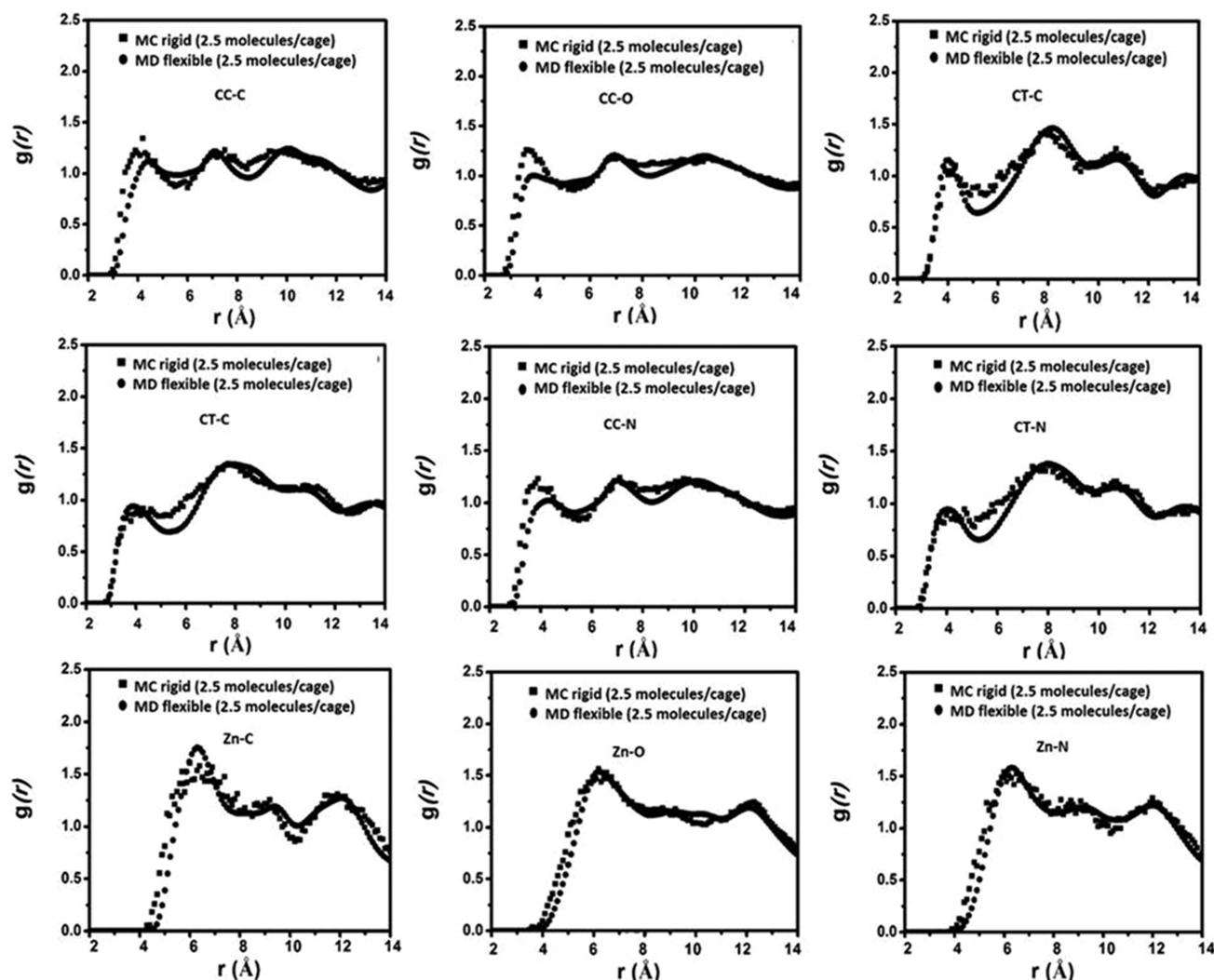
**Figure 5.** Favorite orientation of  $\text{CO}_2$  at adsorption sites inside the ZIF-8 framework.

For the diffusion selectivity it can be seen that  $\text{N}_2$  can diffuse a little bit faster than  $\text{CO}_2$  at all loadings and temperatures. That means that  $\text{N}_2$  can move within the ZIF-8 framework somewhat faster than  $\text{CO}_2$  in the mixture of  $\text{CO}_2/\text{N}_2$ . For numerical values see Table S1 in the [Supporting Information](#). The adsorption selectivity is discussed below.

### 3.3. Adsorption Sites of the $\text{CO}_2/\text{N}_2$ Mixture in ZIF-8.

In [Figure 4](#) RDFs between atoms of  $\text{CO}_2$  with lattice atoms in single-gas  $\text{CO}_2$  and between atoms of  $\text{CO}_2$  and  $\text{N}_2$  in the mixture  $0.5 \text{CO}_2/0.5 \text{N}_2$  in ZIF-8 at low loading are given. It

follows from [Figure 4](#) that the favorite adsorption sites of single-gas  $\text{CO}_2$  and mixed gas  $\text{CO}_2/\text{N}_2$  are positions close to atoms of the organic linkers such as CC and CT (for the meaning of these abbreviations see the lattice fragment picture in [Figure 4](#)). Moreover, the carbon atom C of the  $\text{CO}_2$  molecules as single gas as well as in the  $\text{CO}_2/\text{N}_2$  mixture has a stronger interaction with the ZIF-8 framework than the O atoms of  $\text{CO}_2$  and the N atoms of  $\text{N}_2$ . The RDFs of CC–C and CT–C show sharper peaks than CC–O, CT–O, CC–N, and CT–N.



**Figure 6.** Comparison of the RDF graphs of ZIF-8 (CC, CT, and Zn) and guest molecules (C, O of CO<sub>2</sub> and N of N<sub>2</sub>) from flexible MD and rigid MC.

Additional RDF graphs among all atom types of guest molecules and some RDFs with the ZIF-8 lattice are shown in Figures S1–S4 of the [Supporting Information](#). All RDF results support our interpretation.

The main orientations of guest molecules were parallel with CC and CT of the framework as shown in [Figure 5](#).

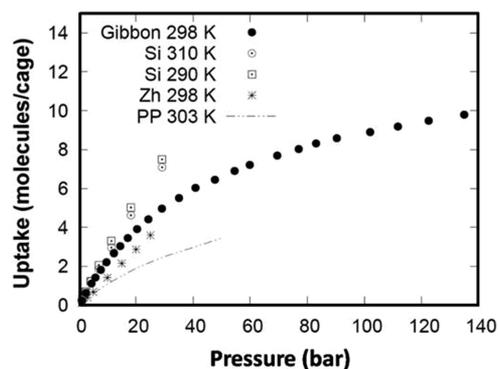
The RDFs for CO<sub>2</sub>/N<sub>2</sub> mixtures at different loading are shown in the [Supporting Information](#). The results give clear evidence for preferential sites and the gate-opening effect because  $g(r)$  of guest molecules still remains nearest at CC and CT positions. With increasing loading of guest molecules, sharp peaks are seen around CC, CT, and Zn. Thus, the strong interaction between CO<sub>2</sub> and N<sub>2</sub> with the organic linker at high loading as shown in the RDF can be important for the rotation of the linker.

**3.4. Comparison of the RDF from Flexible MD and Rigid MC.** For an additional check of the equivalence of flexible MD and rigid MC, the RDFs between the C atom of CO<sub>2</sub> and the lattice CC and the O atom of CO<sub>2</sub> and the lattice CC resulting from the two different simulation methods are compared for the CO<sub>2</sub>/N<sub>2</sub> mixture at a loading of 2.5 molecules/cage. The RDF graphs between ZIF-8 (CC, CT, and Zn) and guest molecules (C, O of CO<sub>2</sub> and N of N<sub>2</sub>) are

shown in [Figure 6](#). These graphs confirm that the structure of the adsorbed phase is found to be similar in flexible MD and rigid MC.

### 3.5. Adsorption Isotherm of Pure N<sub>2</sub> from GEMC.

[Figure 7](#) shows a comparison of the adsorption isotherm for N<sub>2</sub> which is the result of our GEMC simulations employing the



**Figure 7.** Adsorption isotherms for pure N<sub>2</sub> on ZIF-8. Si means Simmons et al. (ref 24), Zh means Zhang et al. (ref 31), and PP means Pérez-Pellitero et al. (ref 23).

interaction parameters that were also used in the MD simulations of the present paper (full dots), with former combined experimental and simulation results. Two isotherms of Simmons et al.<sup>24</sup> obtained at 290 and 310 K show both larger values, whereas the values of Zhang et al.<sup>31</sup> and Pérez-Pellitero et al.<sup>23</sup> are smaller than the values of the present simulations.

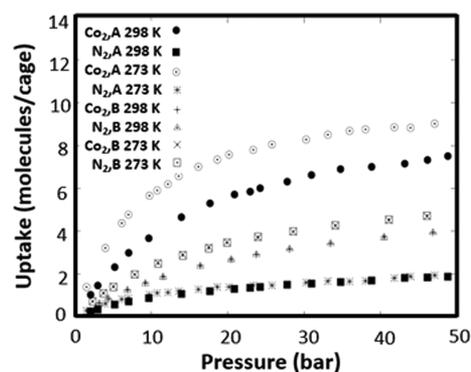
**3.6. Adsorption Behavior of the Equimolar Mixture CO<sub>2</sub>/N<sub>2</sub> from GEMC.** From the low-pressure region of adsorption isotherms published in different papers values of the adsorption constant  $K$  as defined in eq 1 for N<sub>2</sub> and CO<sub>2</sub> in ZIF-8 are extracted. They are compared in Table 1 with corresponding values from our simulations, using the Gibbon software.

The low-pressure results of Simmons<sup>24</sup> for N<sub>2</sub> at 290 K and at 310 K practically agree with each other and have therefore been used here for the comparison with our 298 K results. Note that, in the case of the mixture, the adsorption constant  $K$  has been defined via the partial pressure, not via the total pressure. For the equimolar mixture, the partial pressures at low density are simply half of the total pressure. In the limit of vanishing pressure, the mixture can be regarded as ideal gas and ideal mixture.

From Table 1 it can be seen that large differences between the experimental adsorption results from different papers exist (as stated already by Chokbunpiam et al. for CO<sub>2</sub> in ref 20) and that the Gibbon results using our parameter set, as described above, are near the mean of the scattering experimental values. The values from Zhang et al.<sup>31</sup> that are shown in Table 1 are averaged over the interval 1–5 bar. The reason is that for very low pressures (<1 bar) the isotherm for pure N<sub>2</sub> given in paper 31 shows a strongly nonlinear behavior (see Figure 1 in ref 31). On the contrary, in the range of 1–5 bar (see Figure 6a in ref 31) the uptake seems to be proportional to the pressure like in all other mentioned papers and like in our simulation results for the interval 0 bar <  $p$  < 5 bar. Note that the mixture results of refs 21 and 31 that we used to calculate  $K$  in Table 1 have not been measured or simulated, but they are calculated from pure species data by IAST.

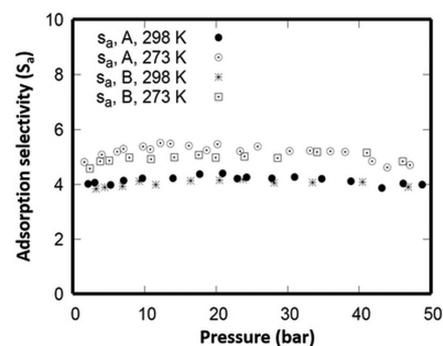
Adsorption isotherms at different temperatures for pure CO<sub>2</sub> have been given by Chokbunpiam et al.<sup>20</sup> They have been calculated using the same parameters for CO<sub>2</sub> and the lattice atoms that are employed in the present paper.

Figure 8 shows the adsorption isotherms for mixtures CO<sub>2</sub>/N<sub>2</sub> at 298 K and at 273 K. Case A means equimolar in the gas phase corresponding to a ratio 4:1 at 298 K and 5:1 at 273 K in



**Figure 8.** Adsorption isotherms for equimolar mixtures CO<sub>2</sub>/N<sub>2</sub>. A means equimolar in the gas phase and B means equimolar in the adsorbed phase.

the adsorbed phase. Case B corresponds to equimolar mixture in the adsorbed phase corresponding to a ratio 1:4 at 298 K and 1:5 at 273 K in the gas phase. In case B, the almost equimolar mixture in the adsorbed phase is constructed by trial variations of the CO<sub>2</sub>/N<sub>2</sub> ratio in the gas phase. The results can be seen in Figure 8. Interestingly, in case A the adsorption of N<sub>2</sub> in this mixture is not much influenced by the temperature change, while the adsorption of CO<sub>2</sub> is enhanced by about 25% by decreasing the temperature from 298 to 273 K. The resulting CO<sub>2</sub>/N<sub>2</sub> adsorption selectivities  $S_a$  can be seen in Figure 9. It



**Figure 9.** Adsorption selectivity CO<sub>2</sub>/N<sub>2</sub> as a function of the gas-phase pressure for equimolar mixtures CO<sub>2</sub>/N<sub>2</sub>. A means equimolar in the gas phase and B means equimolar in the adsorbed phase.

turns out that the selectivity at 273 K is about 5 and at 298 K it is about 4, while the influence of the loading and also of the ratio of the species in the gas phase does not much influence the selectivity.

In Figure 9 of McEwen et al.,<sup>21</sup> the adsorption selectivity CO<sub>2</sub>/N<sub>2</sub> at 298 K and 1 bar as calculated by IAST from pure species adsorption isotherms is given. The adsorption selectivity is low and does not depend upon the CO<sub>2</sub>/N<sub>2</sub> ratio. However, the exact value of the adsorption selectivity is difficult to derive from Figure 9 of ref 21 because of its relatively small value for ZIF-8. The estimated adsorption selectivity in McEwen et al.<sup>21</sup> is of the order of our value, but it seems to be somewhat larger. This is clearly due to the stronger adsorption of N<sub>2</sub> in our model (see Table 1).

In McEwen et al.,<sup>21</sup> the adsorption selectivity CO<sub>2</sub>/N<sub>2</sub> at 298 K is calculated from pure component adsorption data by IAST as a function of the pressure. A slight decrease of the selectivity with increasing pressure has been found. The average value of the selectivity agrees well with our value. Neither in Zhang et al.<sup>31</sup> nor in McEwen et al.<sup>21</sup> have mixture simulations been carried out.

The CO<sub>2</sub>/N<sub>2</sub> adsorption selectivity depends much more on the temperature than on the pressure. For both temperatures it seems to be slightly higher for densities around  $4 \times 10^{-4}$  molecules per Å<sup>3</sup> than for the other densities, but this difference is still too close to the magnitude of the fluctuations to be sure.

We also calculated a predicted membrane selectivity as proposed in refs 9 and 43–45

$$\alpha_{ij}^{\text{membrane}} = (\alpha_{ij}^{\text{diffusion}})(\alpha_{ij}^{\text{adsorption}})$$

with the diffusion selectivity  $\alpha_{ij}^{\text{diffusion}}$  as the ratio of the self-diffusivities of the species  $i$  and  $j$  and the adsorption selectivity  $\alpha_{ij}^{\text{adsorption}}$  as the ratio of the adsorbed amounts of  $i$  and  $j$ .

We investigated at 298 K the mixture equimolar in ZIF-8 at concentrations of 1.25 and 2.5 guest molecules per cage. These

are the two low-pressure cases in Table S1 of the Supporting Information for which we can do GEMC simulations. For 1.25 molecules per cage (at the pressure of 3.2 bar) we find an adsorption selectivity

$$\alpha_{ij}^{\text{adsorption}} = 3.84$$

with  $i$  meaning  $\text{CO}_2$  and  $j$  meaning  $\text{N}_2$ . With the diffusion selectivity (see Table S1 in the Supporting Information)

$$\alpha_{ij}^{\text{diffusion}} = 0.865$$

we find the membrane selectivity  $\alpha_{ij}^{\text{membrane}} = (\alpha_{ij}^{\text{diffusion}}) \cdot (\alpha_{ij}^{\text{adsorption}}) = 0.865 \times 3.84 = 3.32$ . This value is lower than the value 5.72 found by Pusch et al.<sup>33</sup> in the low-pressure limit but closer to the results of Diestel et al.<sup>46</sup> who found in mixed gas permeation on a supported ZIF-8 membrane a separation factor  $\text{CO}_2/\text{N}_2 \approx 2$  from mixed gas permeation studies.

For 2.5 molecules per cage that corresponds to a pressure of 6.88 bar we find an adsorption selectivity of

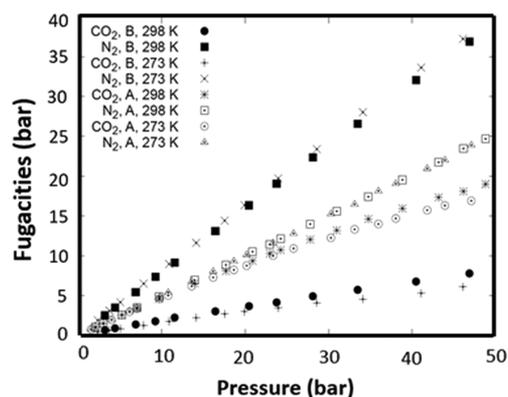
$$\alpha_{ij}^{\text{adsorption}} = 3.93$$

With an diffusion selectivity (from Table S1) of

$$\alpha_{ij}^{\text{diffusion}} = 0.742$$

we find the membrane selectivity to be  $\alpha_{ij}^{\text{membrane}} = 2.92$ . This is in acceptable agreement with results of Diestel et al.<sup>46</sup> who found the membrane selectivity  $\approx 2$  as mentioned above.

Figure 10 shows the fugacities of  $\text{CO}_2$  and  $\text{N}_2$  at 298 K and at 273 K as a function of the gas-phase pressure for both cases A



**Figure 10.** Fugacities of  $\text{CO}_2$  and  $\text{N}_2$  at 298 K and at 273 K as a function of the gas-phase pressure for equimolar mixtures  $\text{CO}_2/\text{N}_2$ . A means equimolar in the gas phase and B means equimolar in the adsorbed phase.

and B of the equimolar mixtures  $\text{CO}_2/\text{N}_2$ . These fugacities are calculated by use of the Peng–Robinson equation<sup>42</sup> for a mixture from the gas-phase densities and the temperature, respectively. For each species the fugacity in the gas phase and in the adsorbed phase is equal in equilibrium. Hence, the GEMC simulation again provides the possibility to calculate thermodynamic quantities for the adsorbed species easily from the gas phase. The fugacity, that at low pressure agrees with the partial pressure for each species, can help to discuss the thermodynamic impact of each species on the lattice. In case B, in which the mixture is equimolar in the adsorbed phase, the fugacity of  $\text{N}_2$  is much larger than that of  $\text{CO}_2$ . That means much higher fugacity is necessary to press the same amount of

nitrogen into the pores. This high fugacity that is similar to a kind of partial pressure can explain that the gate opening in case B is dominated by  $\text{N}_2$  if we assume that also at the high loadings where gate opening happens (and that cannot be realized in our GEMC) the fugacity of  $\text{N}_2$  is still larger than that of  $\text{CO}_2$ . Also in case A, although the mixture in the gas phase is equimolar, the fugacities agree only up to about 10 bar, while for higher pressure the fugacity of  $\text{CO}_2$  increases more slowly. The difference increases stronger than linearly.

## 4. CONCLUSIONS

Molecular adsorption and diffusion of the gas mixture  $\text{N}_2/\text{CO}_2$  in the metal–organic framework ZIF-8 are investigated by using MD and GEMC simulations. The validation of the interaction parameters by comparison with experimental adsorption results shows satisfactory agreement.

While the adsorption of  $\text{N}_2$  was found to be in a temperature window from 298 to 273 K almost independent of the temperature, the adsorption of  $\text{CO}_2$  shows the clear van't Hoff dependence and decreases with increasing temperature, which results in an increasing  $\text{CO}_2/\text{N}_2$  adsorption selectivity with decreasing temperature.

Gate-opening effects as investigated before for single-component gas adsorption could also be observed for the  $\text{CO}_2/\text{N}_2$  mixture in ZIF-8. In the mixture  $\text{CO}_2/\text{N}_2$ , gate opening of ZIF-8 happens at a total amount adsorbed of 20 molecules/cage, while for single-component  $\text{CO}_2$  it happened at 22.5 molecules per cage and for pure  $\text{N}_2$  at 18.4 molecules per cage. The stronger influence of  $\text{N}_2$  on the start of gate opening can be understood in terms of the fugacity of  $\text{N}_2$  that has been found in GEMC for all pressures up to 50 bar for the equimolar mixture in ZIF-8 to be 4 times larger than that of  $\text{CO}_2$ . Note, however, that the gate opening was found at larger pressure that cannot be investigated by GEMC as mentioned. Evaluation of the self-diffusion coefficient and diffusion selectivity from MD and adsorption selectivity from GEMC made it possible to calculate membrane selectivities that agree satisfactorily with experiments.

The strong decrease of the self-diffusion coefficient at high loadings, due to the mutual hindrance of the guest molecules at high occupancy, happened in the mixture at about the same total loadings of guest molecules in comparison to single-gas loadings. Obviously the influence of the mutual hindrance could not be compensated by the gate opening.

Investigations of the structure by RDFs of the adsorbed guest molecules do not show remarkable differences to the structure of adsorbed pure  $\text{CO}_2$ . Favorite adsorption sites of all guest molecules in single-gas  $\text{CO}_2$  and mixed gas  $\text{CO}_2/\text{N}_2$  are positions close to atoms of the organic linkers.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b05506.

Details of the radial distribution functions, self diffusion coefficients, and diffusion selectivities (PDF)

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### Notes

The authors declare no competing financial interest.

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