



# Gate opening effect for carbon dioxide in ZIF-8 by molecular dynamics – Confirmed, but at high CO<sub>2</sub> pressure



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## ABSTRACT

Since the simulation of the CO<sub>2</sub> adsorption in ZIF-8 for the ZIF-8 HP (high-pressure phase) and ZIF-8 AP (conventional phase) structures – as defined in [1] – gave similar results [2], Molecular Dynamics (MD) has been applied to decide which of these two structures exists at which CO<sub>2</sub> pressure. MD simulations with flexible lattice show that a transition from the ZIF-8 AP to the ZIF-8 HP structure takes place at extremely high CO<sub>2</sub> pressure, i.e. at high loading.

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## 1. Introduction

Zeolitic Imidazolate Frameworks (ZIF's) belong to the most promising among the recently developed Metal-Organic Frameworks (MOFs) because of their extraordinary thermal and chemical stability and the huge variety of structures that can be designed [3]. In some of them, structural changes under increased loadings with guest molecules have been observed. E.g. the group of Kapteijn could show in ref. [4] that the separation of an ethane/ethylene mixture could be drastically enhanced since only for ethane the gate opening effect took place. This happened for ethane in ZIF-7 even at room temperature and a low loading of 3.5 molecules per cavity corresponding to a pressure of 10 kPa.

This gate opening leads to wider apertures (windows) between adjacent cavities that allow larger molecules to pass these bottlenecks or to enhance their diffusion inside the MOF framework. In this letter we investigate the possibility of gate opening for CO<sub>2</sub> in ZIF-8 by Molecular Dynamics simulations (MD) with flexible lattice. We define 'gate opening' as the transition of a closed to an open window by conformational change of the linker molecules.

In ref. [5] the existence of two different structural phases of ZIF-8 has been discovered, one phase exists at ambient (AP) and the other phase at high pressure (HP). In [1] these structures are named ZIF-8 AP and ZIF-8 HP, and the comparison of adsorption experiments

with Grand Canonical Monte Carlo (GCMC) simulation shows for the N<sub>2</sub> adsorption using rigid lattice structures that such a structural phase transition (gate opening) from ZIF-8 AP to ZIF-8 HP can happen for N<sub>2</sub> already at ambient pressure.

This finding could be reproduced in MD simulations of N<sub>2</sub> in ZIF-8 with flexible lattice at low temperature, first in ref. [6]. The authors of ref. [6] interestingly applied MD with flexible lattice using DL\_POLY to find the appropriate lattice structure corresponding to a given pressure used in Gibbs Ensemble (GEMC) simulations with rigid lattice. The gate opening for N<sub>2</sub> in ZIF-8 was also found in ref. [7] at ambient temperature. The loading, at which the gate opening effect appeared in [7], agreed well with the experiment.

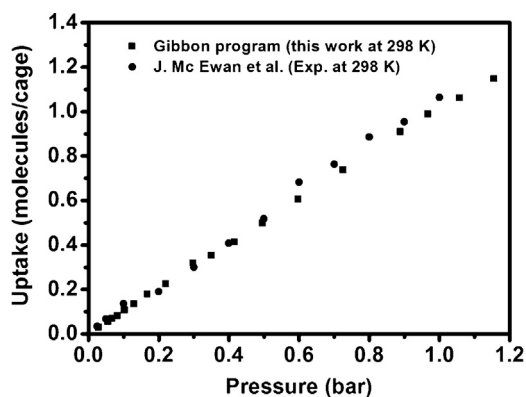
In ref. [2] the simulation of the adsorption of CH<sub>4</sub> and CO<sub>2</sub> in ZIF-8 was compared with experiments. It turned out for CH<sub>4</sub> that in the Grand Canonical Monte Carlo (GCMC) with rigid lattice only ZIF-8 AP at ambient pressure, and only ZIF-8 HP at high pressure gave good agreement with the experimental adsorption data. Hence, a transition between both of these structures was suggested. But, the simulation of CO<sub>2</sub> adsorption in both the ZIF-8 AP and ZIF-8 HP rigid lattice structures reported in ref. [2] gave almost identical results.

Hence, the comparison of these simulation results of adsorption with the experiments could not answer the question if a structural transition takes place for CO<sub>2</sub> and if, at which feed pressure. It is the aim of the present letter to answer these questions.

Interaction parameters used in such a simulation should reproduce both adsorption and dynamical properties like diffusion as well. But – even for adsorption – the choice of interaction parameters is complicated by the fact that several experimental letters showed quite different results for the adsorption of CO<sub>2</sub> in ZIF-8 (see

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**Figure 1.** Adsorption isotherm for CO<sub>2</sub> in ZIF-8 at 298 K from GEMC simulation (own GIBBON software) compared with experimental data [12].

Figure 3). Each of these experimental letters includes also simulations and each letter proposes also a set of interaction parameters that yields exact agreement of simulation results with just this special experimentally measured isotherm.

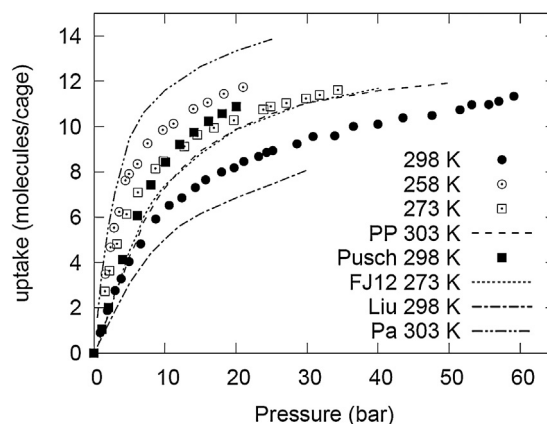
Hence, we decided to consider also the diffusivity in comparison with the experiment as criterion for correct parameter sets, and found that the interaction parameters of the lattice from our earlier letter [7] together with the parameters of ref. [8] for CO<sub>2</sub> gave good agreement with the diffusion experiments of refs. [9–11]. But, also the adsorption isotherm obtained with these parameters is within the range of the different measured isotherms. Therefore, we used these parameters.

For this finally chosen set of interaction parameters, we found by Gibbs Ensemble Monte Carlo (GEMC) simulations in the low pressure region a very good agreement with the experiment of ref. [12] as can be seen in Figure 1.

## 2. Computational details

The structure of Zeolitic Imidazolate Framework-8 (ZIF-8) was obtained from X-ray diffraction (XRD) pattern by Park et al. in ref. [3]. The adsorption calculations have been done by Gibbs Ensemble Monte Carlo (GEMC) [13] using a homemade software, called GIBBON. In GEMC simulations, Metropolis MC is carried out in two simulation boxes. One box contains bulk gas, the other one the ZIF crystal with adsorbed gas molecules. Particle exchange between both boxes is enabled and leads to equilibrium between the boxes. Hence, the bulk gas density that is in equilibrium with a given loading of guest molecules within the ZIF-8 could be evaluated. The pressure was calculated from this gas phase density using the equation of state of Span and Wagner [14] employing the tool offered in ref. [15]. An appropriate box size of the gas box was chosen in order to get the wished pressure for each run. During the run the box size was constant. Then in equilibrium the concentration of guest molecules in the ZIF-8 structure could be evaluated.

In ref. [16] it has been shown for the first time that for many-particle systems, in which the sum of charges is zero and the spatial distribution of charges is roughly uniform, instead of the computer time expensive Ewald summation, Coulomb interactions can be calculated also in models that keep the original Coulomb potential values at small distances while dropping it down to zero smoothly or by shifted forces at large distances. This is similar to taking only the *r*-space part of the Ewald summation, but with large enough cutoff. In many-particle systems this cutoff can be much smaller than for an isolated pair of charges because of mutual partial canceling of contributions coming from unequal charges. The method has meanwhile often been employed *e.g.* in ref. [17]. We applied this method in our GEMC simulations using a cutoff of 30 Å.



**Figure 2.** Adsorption isotherms of CO<sub>2</sub> in ZIF-8. Simulations at 258 K, 273 K and 298 K (this work) compared with experimental values. PP means the isotherm given in ref. [22], Pusch means the isotherm of ref. [10], FJ12 that of ref. [2], Liu that of ref. [8] and Pa that of ref. [23].

The cubic ZIF simulation box size in the GEMC simulations had a fixed edge length of 67.964 Å. After an equilibration period of typically 10<sup>7</sup> steps (up to 5 × 10<sup>7</sup> steps for the high density runs) an evaluation run of 10<sup>7</sup> steps served to sample averages.

The Molecular Dynamics (MD) simulations have been done using the DL\_POLY software. The MD simulation box of ZIF-8 contained 8 unit cells (33.982 Å) and the lattice was treated as flexible using force field parameters from Chokbunpiam et al. [18]. The MD was employed for calculating structural properties and dynamic properties with given loadings of CO<sub>2</sub> inside the framework. Simulation in the isochoric-isothermal ensemble (NVT) was done to equilibrate the system for 5 ns. Afterwards, the production run of 25 ns in the micro-canonical ensemble (NVE) was carried out for studying the window size and diffusion coefficient. Then, we compared the results from all parameter sets of CO<sub>2</sub> [8,19–21] with the experimental data. These MD simulations were done at 300 K, 1 bar, with an integration time step of 2 fs and VDW interaction cutoff 14 Å. The Coulomb potentials were treated with Ewald summation in the DL\_POLY package.

The efficiency of the cutoff method for Coulomb interactions described above strongly depends on applying the cutoff for the whole (in sum neutral) molecule, not for the single partial charges (atoms). Otherwise the balance of charges is disturbed around the cutoff. This possibility is not given in DL\_POLY that we used for MD. So, we must use the computer time expensive Ewald method in MD (or use the worse cutoff atom by atom).

In order to detect a possible gate opening the window size distributions have been examined at different loadings with guest molecules. Since for low loadings no gate opening was found, the simulations have been extended up to high pressures which correspond to high loadings. High pressure investigations for ZIF-8 have already been done before. In ref. [5] the structural phase transition of ZIF-8 has been observed experimentally at 1470 bar under loadings up to 41 methanol molecules per unit cell.

Unfortunately we could not follow the way proposed in ref. [6] to use the structure with open windows for GEMC because for CO<sub>2</sub> in ZIF-8, the transition to the open windows happened at a pressure where the application of GEMC was not possible.

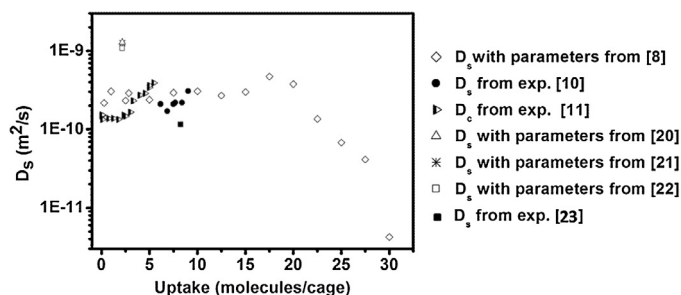
## 3. Results and discussion

The adsorption isotherms at 258 K, 273 K and 298 K as obtained with the GIBBON software using the proposed set of interaction parameters are compared with those of other letters (experiments accomplished by simulations) in Figure 2. These different

adsorption isotherms and simulations do not allow to decide which structure really exists at which gas pressure. Moreover, the proposed parameters for simulation from these letters differ from each other. Hence, diffusion measurements (Pulsed field Gradient NMR self-diffusion and transport diffusion studied by sorption uptake/desorption detected with IR Microscopy) served as a second criterion to find appropriate parameters. Simulations with our finally chosen parameters gave also adsorption isotherms within the range of the measured ones.

For CO<sub>2</sub> at 298 K the phase transition from gaseous to liquid state happens at about 64 bar. Simulations for the phase coexistence in one simulation box cannot be done with our GEMC software because the periodical boundary conditions would produce artificial tiny droplets in the gas phase. In order to avoid artifacts, we did not extend our isotherm simulation to higher pressures. Figure 3 shows a comparison of the diffusivity obtained in this letter by MD simulations using DL-POLY with other letters.

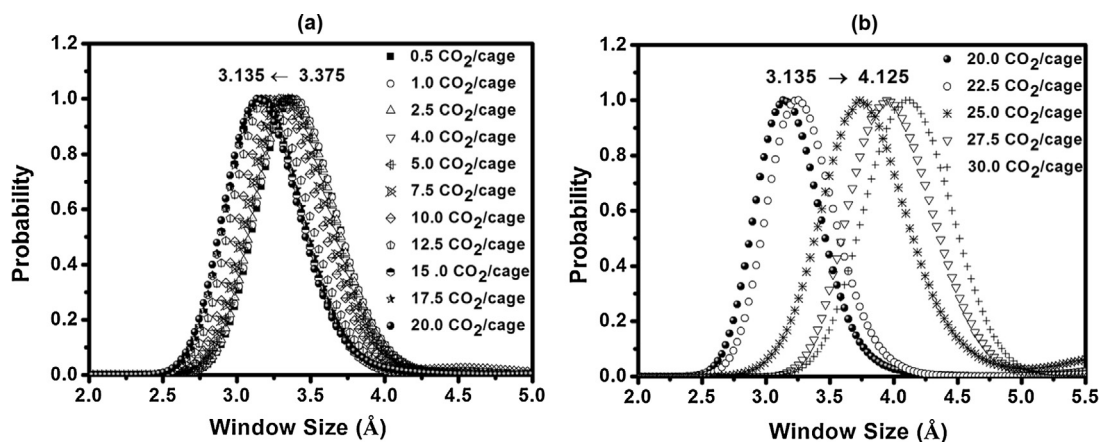
Using the parameters found to be appropriate in the former section the static and dynamic properties of CO<sub>2</sub> in ZIF-8 have been investigated. The CO<sub>2</sub> parameter of Liu et al. [8] (diamond symbols) gave the best agreement with experimental data for the diffusion of CO<sub>2</sub> molecules in ZIF-8 as shown in Figure 3. The  $D_s$  from simulations agreed well with the experiments from loading 0.5 to 10.0 CO<sub>2</sub> molecules/cage. Moreover, it can be seen that the CO<sub>2</sub> self-diffusivity slightly increases from about  $2\text{--}4 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  in the



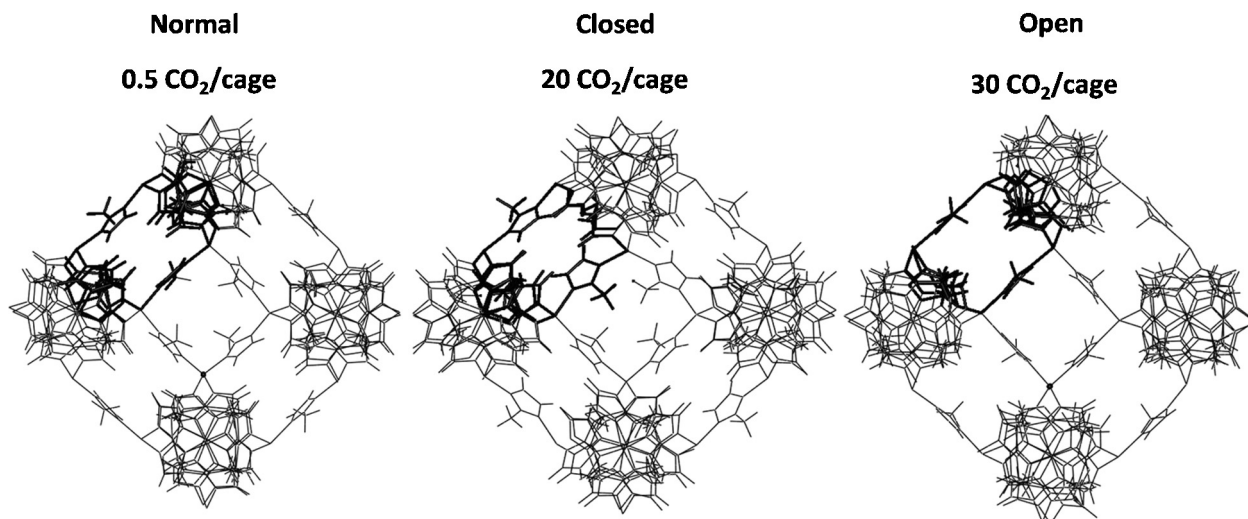
**Figure 3.** The diffusion of CO<sub>2</sub> molecules in ZIF-8 framework by MD simulations at 300 K with different parameter sets and experimental diffusion data obtained in Pulsed Field Gradient NMR and IR Microscopy for comparison.

loading range from 0.5 to 20 molecules/cage. Then, starting at a loading of about 20 CO<sub>2</sub> molecules/cage, a rapid decrease of  $D_s$  is noted for the simulation data. Finally, at 30 molecules/cage the mobility drops below  $10^{-11} \text{ m}^2 \text{ s}^{-1}$ , indicating overfilling of the pores. This trend is very similar to the dependence found for N<sub>2</sub> [7], just the mobility of CO<sub>2</sub> is by the factor of 2–3 smaller.

Qualitatively, the dependence of the window size on CO<sub>2</sub> loading is similar to that of N<sub>2</sub>: a slight decrease of the window size until medium loadings followed by a sharp increase at high loadings. However, for CO<sub>2</sub> the window sizes of the 6-membered rings



**Figure 4.** The distribution of window size (6-membered rings) of ZIF-8 for different CO<sub>2</sub> loadings at 300 K. (a) Decrease of the window size from 0.5 to 20 CO<sub>2</sub>/cage. (b) Increase of the window size from 20 to 30 CO<sub>2</sub>/cage.



**Figure 5.** The change of the window sizes *i.e.* 4-membered (normal lines, foreground) and 6-membered rings (strong lines) of ZIF-8 from normal to closed and to open forms.

were decreasing from 3.375 to 3.135 Å for concentrations of 0.5–20 molecules/cage (Figure 4). This decrease is somewhat more pronounced compared with N<sub>2</sub> [7]. The ZIF-8 structure at 20 molecules CO<sub>2</sub>/cage might even be considered as a third structure in addition to ZIF-8AP and ZIF-8HP (Figure 5). Then, in the range of 20–30 molecules/cage gate opening was found for CO<sub>2</sub> in ZIF-8, evidenced by a dramatic increase of the window size from 3.135 to 4.125 Å (Figure 4). Compared to N<sub>2</sub>, the gate opening is shifted to slightly higher CO<sub>2</sub> loadings. For the highest loadings of CO<sub>2</sub> and N<sub>2</sub> at 30 molecules/cage, the window sizes were 4.125 and 3.585 Å, respectively. Thus, CO<sub>2</sub> causes a remarkably bigger window size than N<sub>2</sub> by around 0.54 Å when gate opening appeared.

Figure 5 shows the structural change of ZIF-8 at high CO<sub>2</sub> loadings. The distribution of the windows diameter of the 6-membered ring – which is the important one for diffusion – as shown in Figure 4, confirms this finding. The linker conformation can be seen in the Figure 5. The importance of the linker molecule methylimidazole for the CO<sub>2</sub> translational mobility was pointed out in refs. [1,23]. As stated in the beginning of the letter, we define ‘gate opening’ as the transition of a closed to an open window at high pressure, *i.e.* high loading, by conformational change of the linker molecules.

#### 4. Conclusions

Taking into account not only adsorption but also diffusion measurements, a better choice among existing interaction parameters could be made to describe these adsorption and diffusion properties of guests in ZIF-8 satisfactorily. This parameter set was then employed to examine in dynamical simulations if a gate opening takes place for ZIF-8 with increasing CO<sub>2</sub> loading. Surprisingly, we found with increasing loading first a decrease rather than an increase of the window diameter up to moderate loadings (up to 20 CO<sub>2</sub>/cage). At very high CO<sub>2</sub> loading from 20 to 30 CO<sub>2</sub>/cage, but still at a guest molecule loading where diffusion is still possible in ZIF-8, such a transition to a structure with open gates finally appears.

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