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# Understanding Inflections and Steps in Carbon Dioxide Adsorption Isotherms in Metal-Organic Frameworks

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The selective adsorption of carbon dioxide from gas mixtures is an important problem in many technical applications, and there is special interest recently due to concerns over greenhouse gas emissions. Metal-organic frameworks are permanently porous coordination polymers that have emerged as an important new class of porous materials that may have a big impact in adsorption separation technologies.[1] The ability to synthesize MOFs with various organic linkers and metal joints provides tremendous flexibility in tailoring the porous material to have specific physical characteristics and chemical functionalities. Information on host−guest interactions and adsorption mechanisms of molecules in MOFs is crucial for developing these novel materials for selective adsorption applications.

Recently, Millward and Yaghi[2] reported room temperature adsorption equilibrium data for $CO_2$ in a large variety of metal-organic frameworks. MOF-177 was shown to have a volumetric adsorption capacity for $CO_2$ that was substantially higher than that of commercial materials such as zeolite 13X and activated carbon powder. Several of the materials exhibited S-shaped isotherms, which were attributed to the very large pore sizes of the MOFs. Other groups[3] have reported $CO_2$ isotherms in MOFs with pronounced steps, which are ascribed to changes in the framework structures, such as a "breathing-type mechanism"[3c] or a "gate effect."[3a] These unusual isotherm shapes are not found for $CO_2$ adsorption in other microporous materials under similar conditions to the best of our knowledge.

In this work, we present experimental adsorption isotherms for $CO_2$ in IRMOF-1 (MOF-5) over a wide range of temperatures. With decreasing temperature, these isotherms exhibit dramatic steps with some similarities to those reported for $CO_2$ in other MOFs.[3] In addition, we present a molecular model that predicts the inflections and steps in very good agreement with experiment and helps explain the adsorption mechanisms that are responsible for this behavior. The molecular model assumes a *rigid* crystal structure and accounts for electrostatic interactions between $CO_2$ molecules by placing point charges on each atom. Similar models have been employed previously for calculating adsorption of $CO_2$ in other MOFs.[4] In this work, we show that the sorbate−sorbate electrostatic interactions are essential for predicting the inflections and steps in the adsorption isotherms in this class of MOFs. All modeling results were obtained from grand canonical Monte Carlo (GCMC) simulations using a consistent set of force field parameters with no adjustable parameters. Full details are given in the Supporting Information.

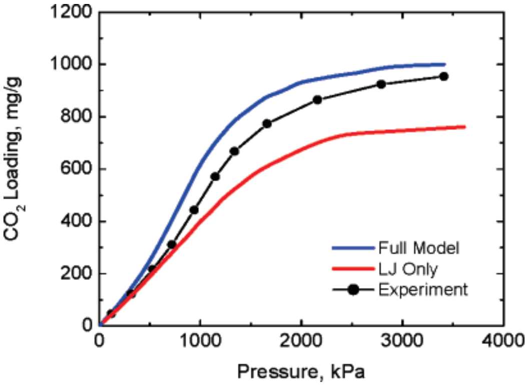

***Figure 1.*** Comparison of GCMC simulations and experimental adsorption isotherms for $CO_2$ in IRMOF-1 at 298 K. The top curve was calculated from a model which included electrostatic effects. The bottom curve was calculated considering only the Lennard-Jones interactions.

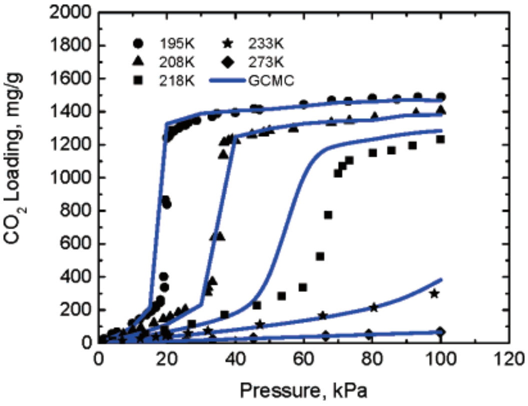

***Figure 2.*** Comparison of GCMC simulations and experimental adsorption isotherms for $CO_2$ in IRMOF-1.

Figure 1 shows the results from two models compared with experiment for $CO_2$ adsorption in IRMOF-1 at 298 K. In the first model, only Lennard-Jones interactions are considered, ignoring the quadrupole moment of $CO_2$. This model predicts saturation loadings that are noticeably lower than experiment. The predicted isotherm also does not possess the inflection point seen in the experimental isotherm. The second model includes both Lennard-Jones and Coulombic interactions. It predicts the saturation loading in better agreement with experiment, and more importantly, it captures the inflection behavior. It should be noted that the inflection

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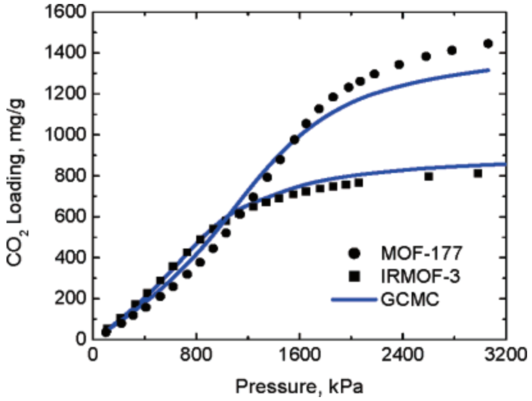

***Figure 3.*** Comparison of GCMC simulations and experimental adsorption isotherms for $CO_2$ adsorption in MOF-177 and IRMOF-3 at 298 K.

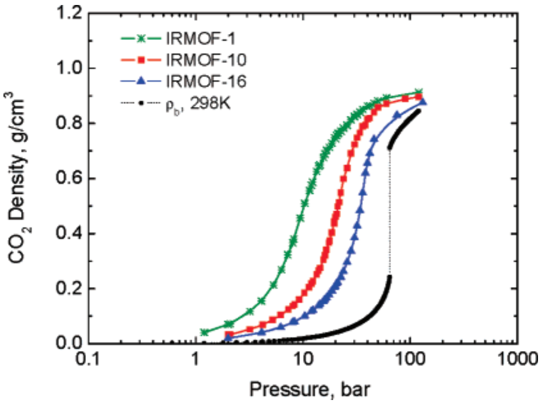

***Figure 4.*** Density of $CO_2$ in IRMOF-1, -10, and -16 compared with bulk values at 298 K. The adsorbed phase densities are calculated considering only the free volumes of the crystal structures.

is captured without invoking any changes in the MOF structure itself. Figure 1 clearly shows the importance of electrostatic interactions between $CO_2$ molecules in capturing the shape of the experimental adsorption isotherm.

Adsorption isotherms for $CO_2$ in IRMOF-1 over a wide range of temperatures are given in Figure 2.[2b] The unusual inflection found in the room temperature isotherm (Figure 1) grows into a very pronounced step at low temperature. Our molecular model provides excellent agreement with the experimental data. The model also works very well for predicting room temperature $CO_2$ adsorption in MOF-177 and IRMOF-3, as shown in Figure 3. In agreement with experiments, the simulations show that the inflections in the isotherms become more defined with increasing effective pore size.

Analysis of the $CO_2$ positions reveals that, below the sharp rise in the isotherms of Figure 2, molecules are mostly adsorbed near the corners of the MOF cavities. With increasing pressure, the pores fill, leading to a type V isotherm.[5] Type V isotherms are relatively rare and are often accompanied by hysteresis.[5] However, neither the experiments nor the simulations display hysteresis. To shed more light on the pore filling, we plotted the density of $CO_2$ within the pore volume of IRMOFs-1, -10, and -16 at 298 K (Figure 4). IRMOF-10 and IRMOF-16 possess approximately double and triple the pore volume per gram of IRMOF-1.[1b] The bulk density of $CO_2$ is also shown in the figure. From these results, we find that the pressure of the pore filling shifts toward the bulk condensation pressure with increasing pore size (IRMOFs-1, -10, -16).

In summary, previously reported steps in the isotherms for $CO_2$ in MOFs were attributed to changes in the MOF crystal structure. However, for the MOFs of this study, we find that attractive electrostatic interactions between $CO_2$ molecules are responsible for the unusual shape of the adsorption isotherms. The isotherm shapes can be predicted by a molecular model using a rigid crystal structure. At 298 K, the pressure at which the pore filling occurs approaches the bulk condensation pressure with increasing pore size.

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**Supporting Information Available:** Molecular model and simulation details; experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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