

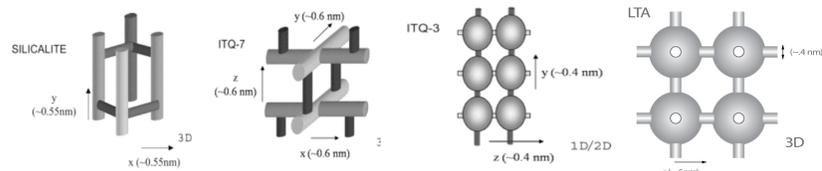
Free Energy Landscape of Orientation for CO₂ and N₂ in the ITQ-3 Zeolite

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Introduction

Zeolites can potentially be used to sequester CO₂ from the atmosphere because they can hold as much as 40 times the CO₂ as the same volume of empty space. Zeolites are porous, crystalline structures. We use atomistic modeling and computer simulations to study the behavior of CO₂ and N₂ in four zeolites, silicalite, ITQ-7, ITQ-3, and LTA, all of which have the same molecular formula, SiO₂. The images above show the void space where adsorbed molecules can be found in the zeolite. While



silicalite and ITQ-7 have channels spanning three dimensions, ITQ-3 and LTA are cage type zeolites that have a one dimensional pore system characterized by narrow hallways connecting large rooms. The location and orientation of N₂ and CO₂ within these materials are important for understanding adsorbate diffusion and selectivity of these zeolites.

Methods

Atomistic Interactions

The zeolite is modeled as a rigid framework with silicon and oxygen atoms having fixed atomic positions. Adsorbed molecules, CO₂ and N₂, are modeled as containing charged Lennard Jones centers and are assumed to be rigid and linear. Adsorbed molecules interact with the adsorbent and other adsorbed molecules in a pair wise fashion. Short range interactions between adsorbed particles and the zeolite are modeled by Lennard-Jones potentials. Long range interactions are modeled by Coulombic potentials^{1,2}.

Computational Methods

Simulations of pure CO₂, pure N₂, and mixtures of CO₂ and N₂ were conducted using Molecular Dynamics (MD) and Grand Canonical Monte Carlo (GCMC).

MD simulates the motion of the adsorbed molecules by calculating the forces acting on the molecule and then using Newton's equations to calculate the new positions after a time step on the order of femtoseconds.

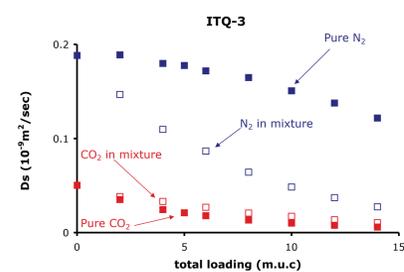
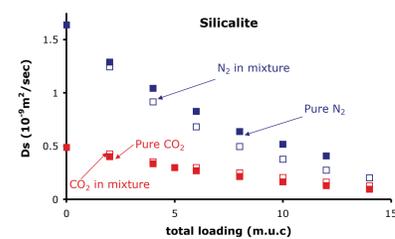
GCMC is a cycle-based method that simulates thermal equilibrium and adsorption within the zeolite. "Actions" include insertion, deletion, translation, or rotation of adsorbed molecules. "Actions" are accepted if they either cause the system to have lower potential energy, or if the probability of the new configuration is larger than a randomly selected number. In this way GCMC simulates thermal equilibrium and not just the lowest possible energy state.

Diffusion for CO₂ and N₂

The self diffusion coefficient (D_s) is the area a molecule explores in a given time period. For random motion at a constant temperature and pressure, the self diffusion coefficient does not depend on time. Einstein's equation for diffusion coefficient is used to calculate diffusion within the zeolite.

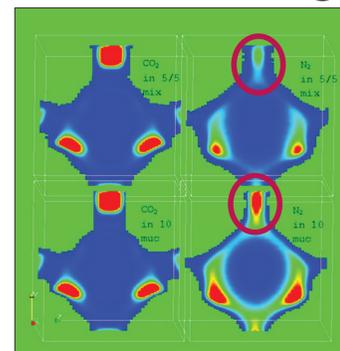
$$D_s = \lim_{t \rightarrow \infty} \frac{1}{6t} \left\langle \frac{1}{N} \left[\sum_{l=1}^N r_l(t) - r_l(0) \right]^2 \right\rangle$$

For silicalite (shown left) and ITQ-7 (not shown), as loading increases, diffusion decreases for CO₂ and N₂.² The trend for diffusion for mixed components is about the same as diffusion for single components.



In ITQ-3 (shown right) the diffusion of pure N₂ does not decrease as rapidly as the diffusion of pure CO₂. However, in the presence of CO₂, the diffusion of N₂ does decrease rapidly. **N₂'s diffusion behaves in a unique way in ITQ-3 compared to its behavior in silicalite and ITQ-7.**

Preferred Siting in ITQ-3



To better understand the behavior of CO₂ and its hindrance of N₂, the siting of CO₂ in ITQ-3 was studied². In the map at left, each quadrant shows a cage (large room) and a narrow channel of ITQ-3 and the probability of locating pure CO₂ (lower left), pure N₂ (lower right) and CO₂ and N₂ in a 50:50 mixture (top, left and right respectively). Red indicates high probability of the adsorbate's being located there.

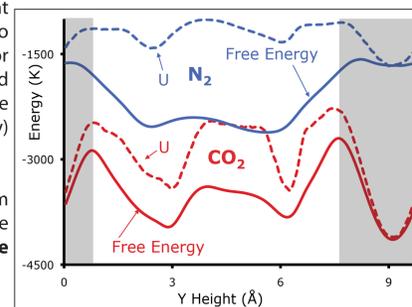
These images indicate that in the presence of CO₂, N₂ is no longer present in the narrow channels between the larger pores. This difference in siting helps to explain why N₂ diffuses differently in the presence of CO₂. **CO₂'s siting in the channel blocks N₂'s movement into the pore.**

Potential and Free Energy in ITQ-3

The free energy and entropy at different locations in ITQ-3's pore structure helps to rationalize N₂'s different diffusion behavior when it is in the presence of CO₂.² As indicated by the graph at right, CO₂ (in red) has a free energy minimum in the channel (shaded gray) where N₂ (in blue) has a free energy maxima.

CO₂'s deep potential energy minimum overcomes the entropic cost created by the channel. **Thus, CO₂ is much more stable in the narrow channel than N₂.**

Furthermore, the barrier to diffusion for CO₂ is at a different location than barrier to diffusion for N₂. CO₂ has a free energy barrier at the entrance of the narrow channel rather than inside the narrow channel as would be expected. In another cage type zeolite, LTA, CO₂ also has diffusion barrier at the entrance to the narrow channel, where as N₂ does not. It is possible that the rotation of CO₂ is associated with the location of the free energy barrier.



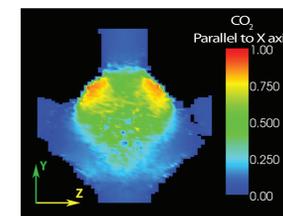
Orientation of Absorbent in ITQ-3

The orientations of adsorbed molecules are being studied to better understand the rotational behavior of CO₂ and N₂ in ITQ-3 and to help explain CO₂'s effect on slowing the diffusion of N₂.

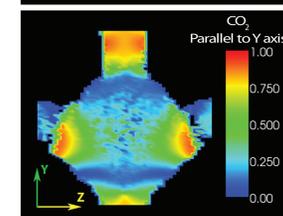
To calculate the most likely orientations of CO₂ and N₂ molecules adsorbed in zeolites, coordinates of all the adsorbed molecules are documented every 10 femtoseconds during an MD simulation. Vectors representing the orientation of the molecules are compared to the the x, y, and z axes.

$$\varphi = \frac{\pi - \theta}{2}$$

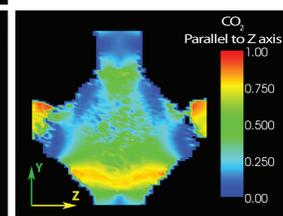
The angle between the vector and the axis of interest, θ , is converted into a value, φ , such that φ is between 0 and 1. When φ equals 1, the vector is parallel to the axis of interest. When φ equals zero, the vector is perpendicular to that axis.



To the left are images that show the average orientation of CO₂ molecules in the zeolite pore. Red indicates those places in the pore where molecules are most parallel to the X (top), Y (lower left), and Z (lower right) directional axes.



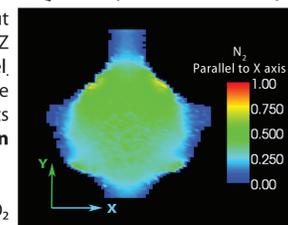
The place in the pore with the highest free energy barrier for CO₂ motion is the place where the opening of the pore intersects with the narrow channel.



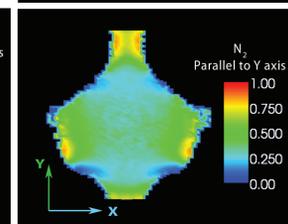
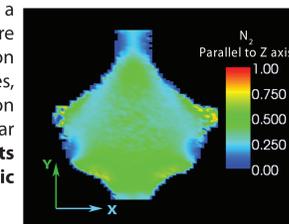
At this place, the average orientation of CO₂ appears to be equally unparallel the all three axes. These plots also reveal that **as a CO₂ molecule travels through the zeolite pore, it takes on different orientations depending on its location.**

Orientation of Absorbent in ITQ-3 (continued)

The images at right show the average orientations of N₂ molecules throughout the zeolite when compared to the X axis (top), the Y axis (lower right) and the Z axis (lower left). Like CO₂, N₂ is more parallel to the Y axis in the narrow channel. However, unlike the orientations of CO₂, the orientations of N₂ throughout the zeolite averages to be about 45° from all three axes. N₂ does not change its orientation as much as CO₂ as it moves through the pore. **CO₂ rotates more than N₂ as it diffuses through the void space of ITQ-3.**



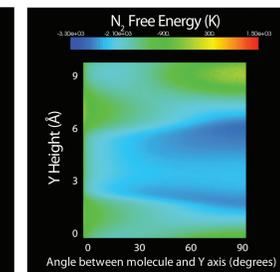
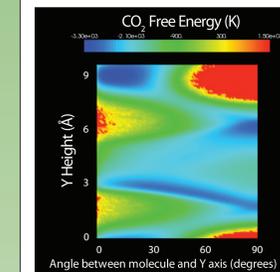
It is important to consider why CO₂ rotates in a unique way compared to N₂. CO₂ is both longer than N₂ and is modeled with a quadrupole that causes it to absorb more strongly to the zeolite structure. CO₂ diffusion was simulated without Coulombic forces, which resulted in the average orientation images (not shown) being qualitatively similar to N₂'s. **CO₂'s rotations are due to its quadrupole and its stronger Coulombic interactions with the zeolite.**



Free Energy of Orientation

One way to understand the rotation of the adsorbate as it diffuses through ITQ-3's structure is to calculate the free energy of the molecule's orientations and location in the zeolite. This method is comparable to the potential and free energy one-dimensional graphs that elucidated the locations of the barriers to diffusion.

Since adsorbate diffuses only in the Y direction, the location of the molecules is simplified to that between the molecule and the Y direction. Free energy was calculated for each Y height and each orientation by the relation free energy is proportional to the ln(Probability).



The images at left show the free energy for CO₂ (far left) and N₂ (near left) and show that inside then narrow channel between Y heights 8 to 9 Å the molecules are most stable (blue) in a Y parallel orientation. CO₂ is especially unstable (red) in the Y perpendicular orientation in side the channel. CO₂ and N₂ cross the threshold of the narrow channel in very different ways. For

CO₂ to enter the large cage structure it cannot simply slide out of the narrow channel in a Y parallel orientation because it hits a free energy barrier. N₂ does not experience such a free energy barrier as it exits the narrow channel. A similar rotation occurs before CO₂ enters the lower channel. **Thus the barrier to diffusion is associated with the rotation of CO₂ before it enters the channel, not simply its movement into the channel.**

To determine the cause of the rotation, CO₂ was simulated without Coulombic forces and the resulting free energy profile (left) confirms that **CO₂ rotates more than N₂ as it diffuses through the zeolite due to the stronger quadrupole and Coulombic forces.**

Future Work

To better understand gas diffusion behavior in cage type zeolites, the orientation studies and free energy profiles will be conducted on simulations of CO₂ and N₂ in LTA. Additionally, the correlation between rotation and translation of adsorbate will be studied with a specific focus on the transition state, where the molecules are at the location in the zeolite associated with the barrier to diffusion.

Acknowledgements

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References

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