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Molecular Insight into CO_2 "Trapdoor" Adsorption in Zeolite Na-RHO

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ABSTRACT: Among other zeolites, sodium-substituted zeolite Na-RHO exhibits a phenomenon known as "trapdoor" adsorption, with extra-framework cations acting as gates to small windows in the zeolite structures. While carbon dioxide can diffuse through these gates, methane and other guests cannot, leading to strong potential for gas separation. This effect has been attributed in the literature to specific cation–guest interactions which would allow to CO_2 to pull the trapdoor open. We investigate here the gating phenomenon using *ab initio* molecular dynamics simulations combined with free energy methods. Our findings invalidate this previously-proposed mechanism, showing that presence of CO_2 does not significantly affect the motion of the gating cation. We put forward and demonstrate an alternative mechanism, showing that the thermal motion of the cations are of large amplitude and that CO_2 is able to squeeze while the gate is open, while nonpolar guests such as methane cannot. This brings an image of the mechanism that is closer to swinging doors than trapdoors.

INTRODUCTION

Effective carbon capture processes require materials with a high ability to discriminate between carbon dioxide and other gases.[1] Microporous adsorbents, such as zeolites and metal–organic framework materials, have received a lot of attention in a drive to reduce greenhouse gas emissions due to their potential applications in gas separation, capture, and storage. These materials are also being studied given their potential applications in catalysis and other gas separation and storage processes.[2-3]

A particularly promising class of materials for carbon capture are those exhibiting cation gating, a phenomenon which allows carbon dioxide but not other sorbents to permeate them. This is the case of some cationic zeolites whose extra-framework cations block the entrances of narrow pores connecting large cages, allowing cations to act as "trapdoors". Only carbon dioxide is then able to diffuse through the materials, bypassing the cations and moving from cage to cage. This cation gating gives rise to very high adsorption selectivities for CO_2 over other small adsorbates, which cannot diffuse through the material.

Some members of the Zeolite RHO and CHA (chabazite) family exhibit this behavior. Lozinska and coworkers[4-6] demonstrated that zeolite RHO materials with a Si/Al framework ratio around 4 have both good CO_2 uptake and high CO_2 selectivity with respect to small molecules like nitrogen, methane, and ethane. Similarly, chabazite zeolites CsCHA and KCHA exhibit remarkably high selectivity of carbon dioxide over methane.[7-9] However, the molecular mechanism by which carbon dioxide passes through narrow pores blocked to other gases by cations is not well understood at the microscopic scale. Studies based on crystallographic and DFT evidence highlight the role of carbon dioxide/cation interaction and the collective effects requiring the presence of several CO_2 molecules for the trapdoor to open.[7-9] However, these approaches cannot take into account the dynamical nature of the phenomenon nor the realistic CO_2 loading in the unit cell. Molecular dynamics simulations, on the other hand, offer an ideal tool to investigate the mechanism at play.

In this work we used *ab initio* molecular dynamics (AIMD) to study at the atomistic level the phenomenon of cation gating in the fully exchanged zeolite Na-RHO (Si/Al = 3.80). This Na-RHO structure is the most studied of the RHO family of zeolites, and the most promising for practical applications due to its selective adsorption properties and low cost. The zeolitic RHO topology[10] (Figure 1) is typical of small-pore zeolites with window dimensions close to the kinetic diameter of the relevant gases and cage sizes that facilitate interaction with the adsorbing molecules. It has a 3-dimensional channel system composed of one-size cavities (α-cages). Each α-cage is connected to six other α-cages by double 8-ring pores (D8R). This connectivity gives rise to two interpenetrated pore systems, which are not interconnected. Na-RHO zeolite is known to exhibit some slight flexibility: when loaded with 1 bar of carbon dioxide the 8-rings are distorted, the α-cages become tetrahedral rather than cubic and the zeolite expands approximately 1.5% (but maintains its symmetry in the $I\bar{4}3m$ space group).[5-6] This can be visualized in Figure 1, as well as in 3D using the CIF files for both structures which we have included as Supporting Information. Lozinska et al. have determined using X-ray diffraction that Na^+ cations preferentially occupy S8R (single 8-ring) sites and S6R (single 6-ring) sites (see Figure 1a), both when loaded with CO_2 or not. The cations that sit in the S8R are the cations that block diffusion within the materials. The Si/Al ratio and site occupancies are such that all narrow pores are likely to blocked.

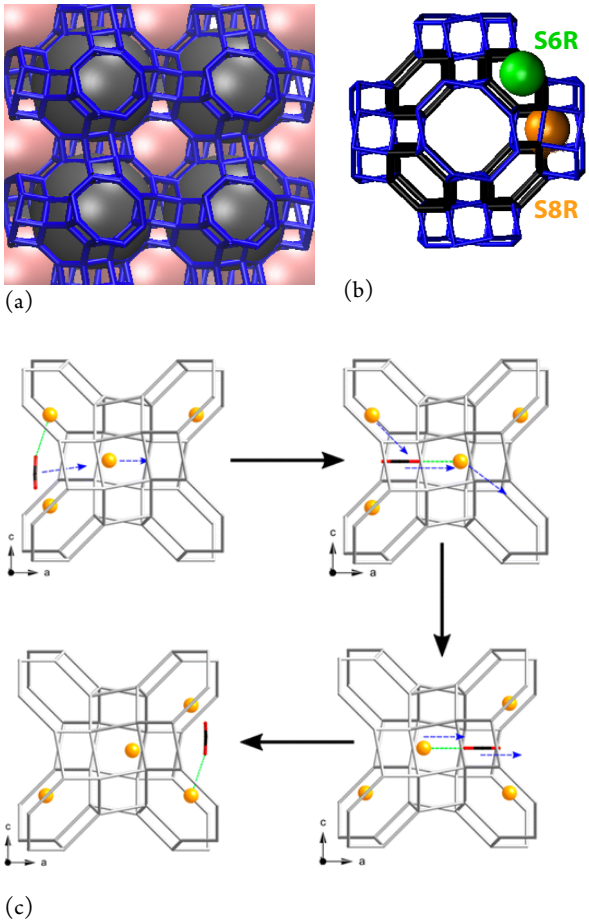


Figure 1. (a) The structure of zeolite Na-RHO when exposed to 1 bar of CO_2. The framework is shown in blue. Note the 3-dimensional channel system composed of cavities (α-cages). Each α-cage is connected to six others by double-8 rings (D8Rs). Shown in grey and pink spheres are cages belonging to the two interpenetrated but not interconnected pore systems. (b) Representation of the Na^+ cation sites. Spheres showing preferred cation sites: S8R in orange and S6R in green. The figure also shows the D8R traced in blue and the S6R traced in black. Each unit cell has 6 D8R sites (and thus 12 S8R) and 8 S6R. The structure shown is that of the empty zeolite; comparing (a) and (b) note the slight distortion that happens upon carbon dioxide adsorption. (c) This figure shows the mechanism proposed by Lozinska and coworkers[5] at low carbon dioxide coverage. It has been reproduced with permission from their article. Note how in this mechanism the blocking cation first moves from one S8R site to its partner S8R site and then to a S6R site to allow for the passage of CO_2. The green lines are meant to emphasize the role of the cation-carbon dioxide interaction (which Lozinska et al. presume would have an even larger stabilizing role in the presence of more carbon dioxide molecules).

Previous work on carbon dioxide within this zeolite using classical molecular dynamics, based on an empirical force field and a rigid description of the zeolite framework, suggested that electrostatic interactions between CO_2 and zeolite produce a favorable binding site beyond the gate. This would opportunistically allow CO_2 to partly enter the channel as the cation gate undergoes thermal fluctuations — although no actual crossing of the window was observed.[11] Figure 2 shows a rare event observed during classical simulation as the carbon dioxide molecule enters a D8R blocked by a cation (in blue). Presumably the fact that other guest molecules lack such strong interaction with the zeolite, result in their incapability to squeeze by the gating cation. These observations hint at a mechanism that differs from the one suggested earlier (see figure 1c) in that the crucial interaction is that of the carbon-dioxide/zeolite and thus the CO_2 does not have an active role on moving the blocking Na^+ out of the way and into a different site.

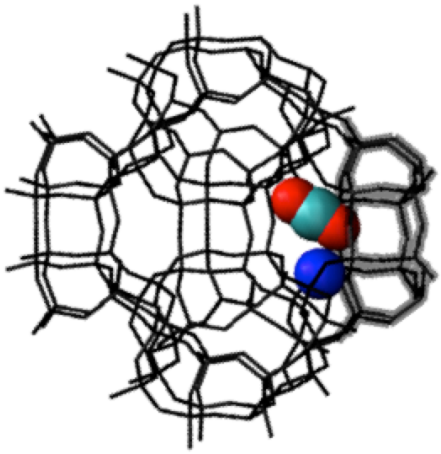


Figure 2. A hint of the microscopic mechanism for gating, observed from classical MD simulations: a carbon dioxide molecule entering a double 8-ring (D8R) blocked by a cation (in blue). Only the relevant adsorbate molecule and cation are shown in the figure (there are 9 more cations and 14 more guest molecules in the classical md simulation). The blocked D8R is highlighted.

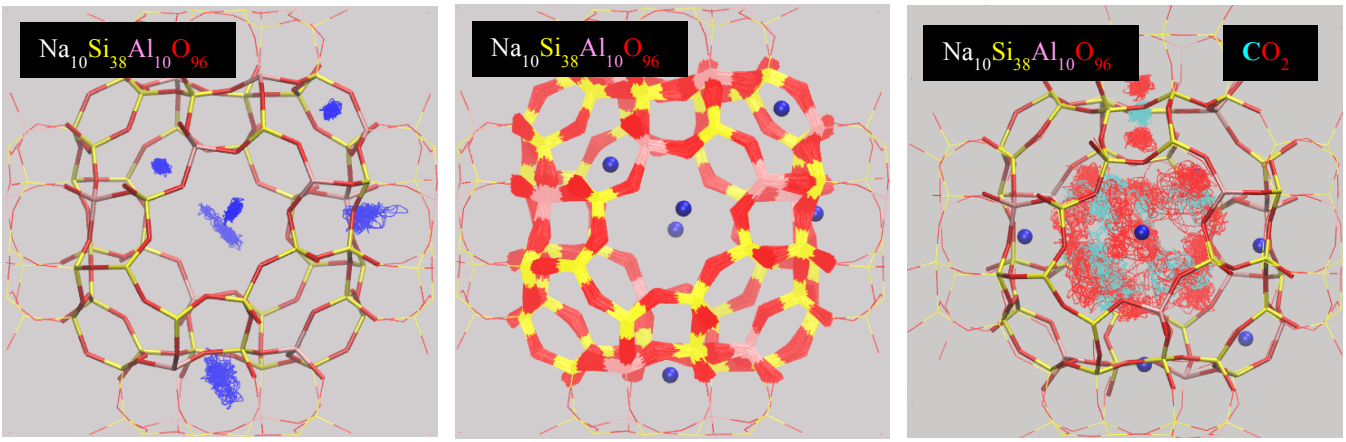
To get a good understanding of the mechanism for cation gating at a microscopic level, we need to go beyond the limitations of classical simulations or time-indepent experimental results. Given the inherent difficulty of obtaining experimental mechanistic information at the microscopic scale, we turned to high accuracy computational condensed matter simulations. Computational advances now make this type of system tractable for *ab initio* molecular dynamics (AIMD), and several studies have highlighted the potential of AIMD to shed light into framework–guest and cation–guest interactions in cationic zeolites.[12-14] Below we present our results using AIMD to further demonstrate carbon dioxide's unique "gate opening behavior" in which its preference for binding inside the "gate" allows CO_2 to "squeeze" by the thermally fluctuating gate-keeping cation.

RESULTS AND DISCUSSION

Ab Initio Molecular Dynamics

We first performed unconstrained (free) *ab initio* molecular dynamics simulations of the Na-RHO zeolite, both without any guest molecules and loaded with 15 molecules of CO_2 — which corresponds to a pressure of 1 atm of CO_2 (See Computational Methods section for details). Figure 3 gives the reader a qualitative idea of the region of space sampled by each atom in the system. Figures 3a and 3b correspond to the same representative trajectory simulating a Na-RHO zeolite without any adsorbate, showing the average positions of all atoms (balls and cylinders) as well as trajectories of individual species (thin lines: Na^+ in Fig. 3a; framework atoms in

Fig. 3b). Figure 3c corresponds to another representative trajectory simulating the Na-RHO zeolite loaded with carbon dioxide. We can see while framework atoms vibrate around their equilibrium positions, the sodium cations show relatively large amplitude of motion (up to 1 Å depending on the particular site) around the S8R and S6R sites, with locations that correspond well to the experimental crystallographic sites presented by Lozinska et. al.[6] (see SI). Finally, we note that carbon dioxide molecules sit preferentially on the S8R but also explore the cage, also in agreement with experimental evidence.



(a) (b) (c)

Figure 3. Representative *ab initio* molecular dynamics trajectories. a) System without guest molecules, with blue traces corresponding to the cation motion. For clarity only cations adsorbed on the central cage shown are displayed, and the rest of the zeolite is shown at its average positions. b) System without guest molecules, with traces corresponding to the motion of framework atoms; the cations are shown at their average positions. c) Na-RHO zeolite under 1 atm of carbon dioxide. For clarity only molecules adsorbed on the central cage shown are displayed; the rest of the zeolite is shown at its average positions.

In order to provide a quantitative analysis of atomic motion, and to look for vibrational modes that could correspond to a concerted motion involving the blocking cation and carbon dioxide, we analyzed the AIMD trajectories using the effective normal modes method.[15] The details of this analysis are shown in SI, and show that there is no unique vibration mode responsible for the gating phenomenon. Instead, we find that there are about 120 modes that invoke significant cation motion. With only 10 cations in the system, these modes also have contributions of many other atoms and correspond to heavily delocalized motions (e.g., "window breathing") that are a generic feature of zeolite frameworks.[13]

Given that a CO_2 molecule entering the narrow pore or a cation moving from one site to another are likely to be rare events, it not surprising that there were not seen in the unconstrained simulations presented here. The computational demands of AIMD are such that free simulations long enough to witness one are prohibitive. To capture the mechanism we thus turned to free energy calculations using constrained molecular dynamics and the blue moon ensemble method[16-17] (see the Computational Methods section for details).

The mechanism governing the passage of carbon dioxide — unlike other gases, such as methane — from cage to cage in Na-RHO despite the presence of the blocking cation can be uncovered by evaluating the height of the free energy barriers involved. To circumvent the fact that an unconstrained MD simulation is very unlikely to sample a point high on the barrier, we use constrained *ab initio* molecular dynamics to "force" the system to cross the barrier. Following the blue moon approach, averaging the constraint forces gives a quantitative indication of how stable that particular configuration is, and integrating these forces along the reaction coordinate gives the configuration free energy as a function of constraint coordinate.

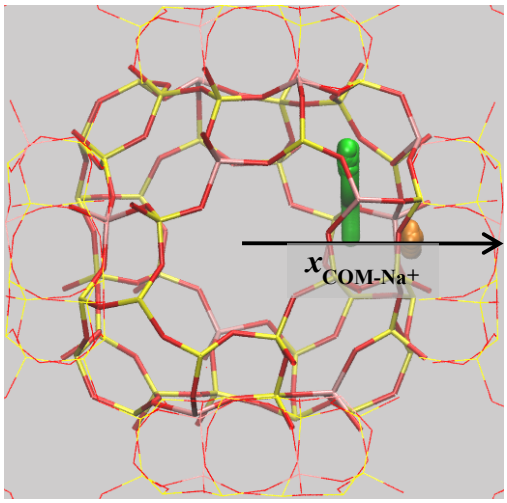
Free Energy Profile: Sodium cation leaving the blocking S8R site

Previous literature on cation gating in Na-RHO suggests[5-6] that the interaction of carbon dioxide with a blocking Na^+ cation allows it to "pull" the cation away briefly from the S8R site and into the S6R site. It is then suggested that during this brief interval CO_2 enters the narrow pore. This scenario can be investigated by evaluating the free energy barrier for a cation to move from the blocking S8R site into the cage and onto a S6R site, in the presence and in the absence of carbon dioxide. For the suggested scenario to be confirmed the barrier must be significantly lower in the presence of guest molecules.

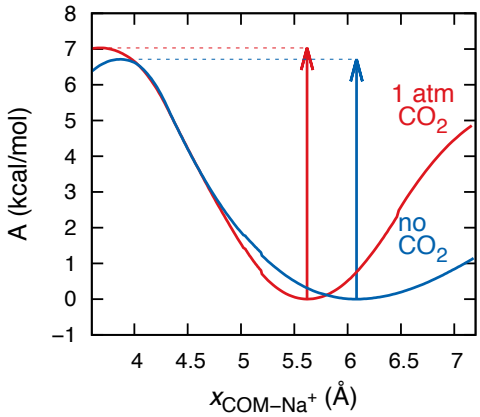
We thus compute free energy profiles as a function of the Na^+ cation coordinate perpendicular to a S8R plane, which corresponds to the direction of the cation leaving the S8R. This reaction coordinated, which we denote by $x(\mathrm{COM–Na^+})$, correspond to the projection of the Na^+ cation's position on the x axis — as depicted in Figure 4a — while the cation is allowed to move freely in the yz plane. For convenience, its zero is chosen as the center of mass (COM) of the zeolitic framework.

The free energy profiles of the Na^+ cation along this direction, both with and without CO_2, are plotted in Fig. 4b. They were obtained by running a series of constrained MD simulations with different values of $x(\mathrm{COM–Na^+})$. Apart from the constrained cation, all other atoms in the system were allowed to move freely. It shows a

range of 3.6 Å ≤ x(COM–Na^+) ≤ 7.2 Å, where the first value corresponds to a cation that has access to the nearest S6R site (figure S3) and the second value to the edge of the unit cell (and thus the midpoint between the two S8R that make a D8R)



a)



b)

Figure 4. a) Scheme of the reaction coordinate corresponding to a cation leaving the single 8-ring (S8R). For convenience the zero was chosen as the center of mass of the framework. Orange corresponds to the trajectory of a cation constrained to x(COM–Na^+) = 5.76 Å and green to a cation constrained at x(COM–Na^+) = 3.6 Å. The trace corresponds to the constrained trajectory (moving only in the *yz* plane) in the absence of adsorbed molecules. b) Free energy profile for a cation leaving the S8R site. Blue line: profile in the absence of carbon dioxide; red line: $P(CO_2)$ = 1 atm.

Figure 4b shows the free energy profiles obtained in the absence and in the presence of 1 atm carbon dioxide. It is clearly visible that that the free energy barrier is not significantly smaller when there is carbon dioxide present (7.0 kcal/mol vs 6.7 kcal/mol). Thus, the calculated free energy profiles indicate that carbon dioxide molecules do not facilitate the movement of the Na^+ cation out of the S8R site. This is in contradiction with the mechanism proposed in earlier work, based on zero-Kelvin DFT calculations of the energy of cation displacement. This highlights the need to account for thermal effects and entropy, as done in our molecular dynamics simulations and through the use of free energy methods.

The free energy profiles do show however that, in the presence of CO_2, Na^+ cations are less likely to migrate to the partner S8R (the ring that makes a D8R with the ring where the cation sits) which we denote S8R*. Moreover, the site they occupy is displaced by 0.5 Å into the cage (from x = 6.1 Å to x = 5.6 Å), and the free energy well becomes more symmetric. Figure 3c points to the reason behind this behavior: D8R contain a cation sitting on a S8R and a carbon dioxide sitting on S8R*, with an optimal Na^+–CO_2 distance "pushing" the cation slightly due to their interaction. This is confirmed by visual inspection of the constrained trajectories, highlighting the formation of CO_2/Na^+ pairs in D8R.

It should finally be noted that the validity of these arguments rests on the appropriateness of the coordinate being used for the free energy profiles. When carbon dioxide is present the "true" reaction coordinate is likely to depend also on the positions of the adsorbed molecules. However the data presented here indicates that the mechanism is not likely to be that of carbon dioxide molecules interacting with a cation in a way that facilitates the opening the trapdoor. We thus turn to explore another option for the mechanism at play.

Free energy profile: CO_2 molecule entering the S8R

From the mechanism hint gathered from classical simulations presented in the introduction (and depicted in Figure 2) and the free energy profile just presented, it appears worthwhile to study how the free energy profile of a guest molecule entering a S8R from the cage is affected by the presence of a nearby cation. Moreover, we note in Fig. 3a that Na^+ has a relatively large amplitude of motion, and from Fig. 4b we see that 2 kcal/mol allow a cation to move from its S8R site into the cage by ~1 Å. Thus at 298 K about 3% of the time the trapdoor is a little ajar, simply by means of thermal motion. Of course, a similar fraction of the time the cation would be exploring the space further from the cage, moving towards the partner S8R*. In the presence of carbon dioxide this other ring is likely to be occupied by another carbon dioxide and thus it is not likely that such an "exploration" would result in an opening for a passing adsorbate.

We thus calculated the free energy profiles for a carbon dioxide molecule entering the narrow pore from the cage, in two different situations: first, when a cation is sitting in its S8R site, with a constrained coordinate of x(COM–Na^+) = 5.76 Å; secondly, when the cation is displaced, with a constraint at x(COM–Na^+) = 4.68 Å. For both situations, the free energy profiles for CO_2 were calculated as a function of the x-axis projection of the COM of the carbon dioxide (with the origin still set at the COM of the zeolitic framework). The free energy profiles for CO_2 are plotted in Figure 5a. Immediately it is clear that a modest displacement of the sodium cation leads to a significant decrease, by a factor of 2, of the free energy barrier for carbon dioxide to enter the ring (from 11.6 kcal/mol to 6.2 kcal/mol). *This decrease and the low value of the resulting free energy barrier, are key to explaining the observed diffusion of CO_2 and the gating phenomenon.* The large amplitude of the thermal motions of the Na^+ out of its crystallographic position allows the carbon dioxide to diffuse through.

The profiles in this case have been extended beyond the limit of the unit cell to allow for the fact that there is no symmetry between the two partners SR8. On the cage side there is a cation siting on (or

near) the ring, while this is not the case on the other side. The minima at ~9 Å correspond to the stable S8R site for carbon dioxide. The fact that carbon dioxide has a stable site on the S8R is crucial to the understanding of the process. It is only because this is the case that the carbon dioxide is able to squeeze by the cation while the latter is out of its equilibrium position. Fig. 5c shows a free energy profile for carbon dioxide obtained when no cation was constrained so all Na^+ were allowed to evolve freely and none was occupying the relevant narrow pore. The profile clearly shows that the S8R is a favorable site for a carbon dioxide.

Moreover, visual inspection and comparison of the geometry of the framework when the CO_2 is outside the S8R or constrained inside reveals that deformation of the framework, in the vicinity of the S8R, is necessary for the guest molecule to pass. The S8R aperture, measured in the narrowest dimension as the center-to-center distance between the two closest oxygen atoms, changes from an average value of 5.27 Å (when the CO_2 is not in the S8R) to 5.57 Å (when the CO_2 is passing through the S8R).

Finally, we tested our explanation of the mechanism by comparing the situation of carbon dioxide with that of methane, which is experimentally known not to permeate the material. We thus calculated the free energy profile for a methane molecule entering the S8R when the gate was partially open, i.e. with a Na^+ cation constrained at $x(\mathrm{COM–Na^+})$ = 4.68 Å. Figure 6b shows that the barrier is significantly higher for methane than for carbon dioxide, in agreement with the experimental results. Furthermore, inspection of Fig. 5c, which was obtained when all cations were allowed to move freely and there was no cation in the D8R of interest, reveals that even in the absence of a cation the barrier for methane diffusion is rather large, much larger than that of carbon dioxide. Both findings are explained by the relatively low affinity of methane for the S8R, irrespective of the presence of a cation: methane sits preferably in the cage rather than in the rings, which are favorable for CO_2 only because of electrostatic interactions.

Finally, we note that the diameter of the narrow pore within Na-RHO obtained using geometric criteria is only 1.9 Å. This is smaller than the kinetic diameter of both CO_2 (3.3 Å in the narrowest dimension) and CH_4 (3.8 Å). [18] Clearly, just looking at the size of the molecules and the pores is not a reliable indicator of the dynamical behavior of the system. The exclusion of methane cannot be accounted for merely by its size, but of its lack of favorable electrostatic interactions with the host material in the single-eight ring. The difference in size of the adsorbate molecules, however, raises the possibility that size or shape selectivity play a role.

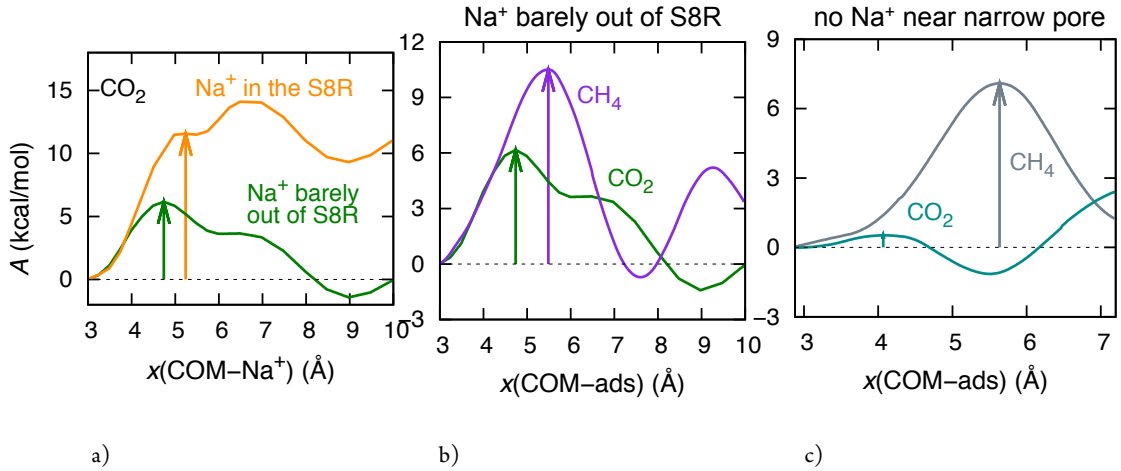


Figure 5. Free Energy Profile for a guest molecule entering the single-8 ring (S8R). a) Results for CO_2 obtained when a cation is constrained to be at $x(\mathrm{COM–Na^+})$ = 5.76 Å (S8R) in orange and when the cation is constrained $x(\mathrm{COM–Na^+})$ = 4.68 Å in green. b) Profile when the cation is constrained at $x(\mathrm{COM–Na^+})$ = 4.68 Å and thus the cation is out of its equilibrium position, carbon dioxide results are shown in green while those of methane are in purple. c) Profiles obtained when all cations can move freely (and none of them was located in a blocking position). Grey shows the methane results while aqua show carbon dioxide results.

CONCLUSIONS

We demonstrated here how the interaction of carbon dioxide with the zeolite Na-RHO's single eight ring (S8R) allows it to enter the narrow pore from the cage as the cation thermally fluctuates in and out of its blocking site. In this microscopic picture of the mechanism for selective CO_2 adsorption, the sodium cations in the rings act as swinging doors agitated by thermal motion, through which the carbon dioxide can squeeze while they are ajar. Methane, lacking the strong adsorbate/zeolite interaction and thus an adsorption site at the gate entrance, experiences a much larger barrier even when the cation is a bit out of the gate. This is the root of the colossal selectivity reported experimental in earlier work.

As there is no experimental data providing direct proof of the diffusion mechanism, we used computational molecular simulation techniques to observe this mechanism. We relied on first principles molecular dynamics simulations of the fully flexible material, combined with free energy methods to obtain free energy profiles as a function of several relevant reaction coordinates —involving of the diffusing guest adsorbate and the blocking cation. To avoid the unfeasibly high computational cost of 2D free energy methods, we calculated cross-sections of this 2D free energy surface by combin-

ing constrained dynamics and the blue moon ensemble. This allowed us to reveal the microscopic mechanism at play.

This mechanism is schematized in the TOC. To move from one cage to another, a carbon dioxide approaches a narrow pore on the side of a S8R occupied by a cation that has thermally fluctuated a bit out of its site. This carbon dioxide squeezes into the pore via an activated process and then moves onto the partnering S8R*. Afterwards, the carbon dioxide can overcame the small barrier that separates the S8R* site from the cage on the right, and thus diffuse through the "blocked" the D8R.

This systematic study on zeolite Na-RHO underscores the power of *ab initio* molecular dynamics combined with free energy methods to study activated events such as guest diffusion in narrow pores blocked by cations. It is entirely transferable to other materials, with different zeolitic frameworks, different cations, or different adsorbate molecules. We expect this *ab initio* methodology to open the way to a more accurate description of guest diffusion at the microscopic level. Moreover, the main conclusions reached here on the importance of cation thermal motion and zeolite/carbon dioxide interactions shed a new light on previous models of narrow pore diffusion in zeolites. The mechanism observed is not specific to Na^+ or the RHO framework, and we expect that it could be observed for other cationic zeolites with narrow windows such as CHA or LTA. However, the quantitative details of the cation's thermal fluctuation motions, zeolite window size, and cation–CO_2 interactions will in each case depend on window size, cation size and cation polarizability.

It puts in perspective the importance of the cation-carbon dioxide interactions, on which many theoretical studies focus but which may not always be a crucial factor limiting diffusion. We have shown that the cation trapdoor is very often a little open, even in the absence of guest molecules. Carbon dioxide molecules are unlikely to facilitate this behavior but they are likely to use the opportunity to get into the almost nominally blocked narrow pore, unlike other adsorbates that lack the preference for that narrow location. In the future, we intend to look at previously proposed diffusion mechanisms of polar species in narrow-pore zeolites to reanalyze them in light of our new findings. We also note that the molecular dynamics simulations and free energy studies performed in this work deal with the {adsorbent, adsorbate} system at or near thermodynamic equilibrium — whereas in industrial fixed-bed gas separation processes, kinetics might play an additional role in the permeation of small molecules. Molecular simulations at a higher scale, or mesoscopic modelling, would be required to study the influence of kinetics on dynamic separation of gas mixtures.

COMPUTATIONAL METHODS

The *ab initio* molecular dynamics simulations were performed using the CP2K simulation package,[19] which uses density functional theory to calculate atomic forces "on the fly". Its QUICKSTEP module uses the Gaussian and Plane Wave (GPW) method[20] or a Gaussian and Augmented Plane Wave (GAPW) method,[21] where the electronic density is expanded on a basis of plane waves. In the work presented here the use of the GAPW scheme for the O and Na atoms and the GPW scheme for Si, C and H atoms resulted in well-converged forces using a 300 Ry cutoff. We use the Perdew-Burke-Ernzerhof (PBE) functional[22] and D3 dispersion correction from Grimme.[23] The core electrons are treated with the Goedecker–Teter–Hutter pseudopotentials.[24] To avoid unphysical charges the sodium atoms were represented by DZVP MOLOPT SR[25] basis sets while all other atoms were represented by TZV2P[25] basis set. The nine outer electrons of Na were treated explicitly, but for all other atoms only their valence electrons were.

The motion of nuclei follows Newton's equation of motion with a time step of 0.5 fs. At each time step, the wave-function is optimized with the self-consistent field convergence criterion set to 1.0 $\times 10^{-6}$ a.u. Simulations were performed in the NVT ensemble with a CSVR thermostat,[26] with a time constant of 100 fs. All simulations correspond to 298 K, the temperature at which carbon dioxide behavior within this material was studied experimentally.

Seven trajectories of at least 25 ps where obtained for an empty Na-RHO and seven others with 15 carbon dioxide molecules (the loading at 1 atm, the pressure at which experimental data is available). In all cases one unit cell was simulated and periodic boundary conditions used. The initial positions for the cations and adsorbates used to start AIMD simulations were obtained using classical Grand Canonical Monte Carlo simulations while the framework atoms were those determined experimentally. The empty zeolite initial positions and those for the zeolite loaded with guest molecules are those of ref. [6]. The methods used are described in Bamberger[11] but briefly note that the interactions between carbon dioxide and Na-exchanged zeolite were modeled using the CCFF potential[27] recently developed by Sholl and coworkers. This potential necessitates a rigid framework but allows the cations to move. More details on the initial configurations can be found on the SI.

As mentioned earlier, free energy profiles were obtained using constrained dynamics and the blue moon ensemble method. [16-17] To compute a free energy profile, at each point along the reaction coordinate the ensemble average force due to the constraint along the constraint direction was evaluated. When the constraint is a simple distance constraint like the one used in our work the average force can be related to the change in free energy by $\frac{dA}{d\zeta_*} = -\langle f \rangle_{\zeta_*}$. Here f is the force due to the constraint along the constraint direction and ζ^* is the value of the constraint (fixed during a given simulation). The free energy as a function of the reaction coordinate (the free energy profile) is then obtained by integrating the average force along the reaction coordinate.

The constrained *ab initio* molecular dynamics simulations were performed using the CP2K code and the parameters detailed above, with constant temperature and fixed unit cell parameters. Note that CP2K computes f at each time step, as it is the Lagrange multiplier in the SHAKE algorithm used to constrain the dynamics. To avoid strong oscillations in f the shake error was required to be less than 10^{-8} a.u. In all cases the forces were averaged after 0.5 ps of evolution to capture the system after it had equilibrated. Errors reported correspond to standard deviation errors and were calculated using the block average method with 10 blocks (errors shown in the force graphs in the SI). A quadratic interpolation scheme was used to integrate the forces and thus to obtain the free energy profiles shown. The center of mass of the guest molecules was used to compute ζ^* to avoid fluctuations related to rotations of the molecules. Care was taken to locate the constraint cation or molecule within the unit cell (avoiding the need to use the periodic boundary conditions in the evaluation of f). The initial configurations were chosen so the cations and guest molecules that were not constrained were relatively well equilibrated with the constrained object. More details are given in the SI.

ASSOCIATED CONTENT

Supporting Information

Cation and carbon dioxide locations. Effective normal modes. Free energy profiles. Details on the generation of initial configurations for AIMD. The Supporting Information is available free of charge on the ACS Publications website.

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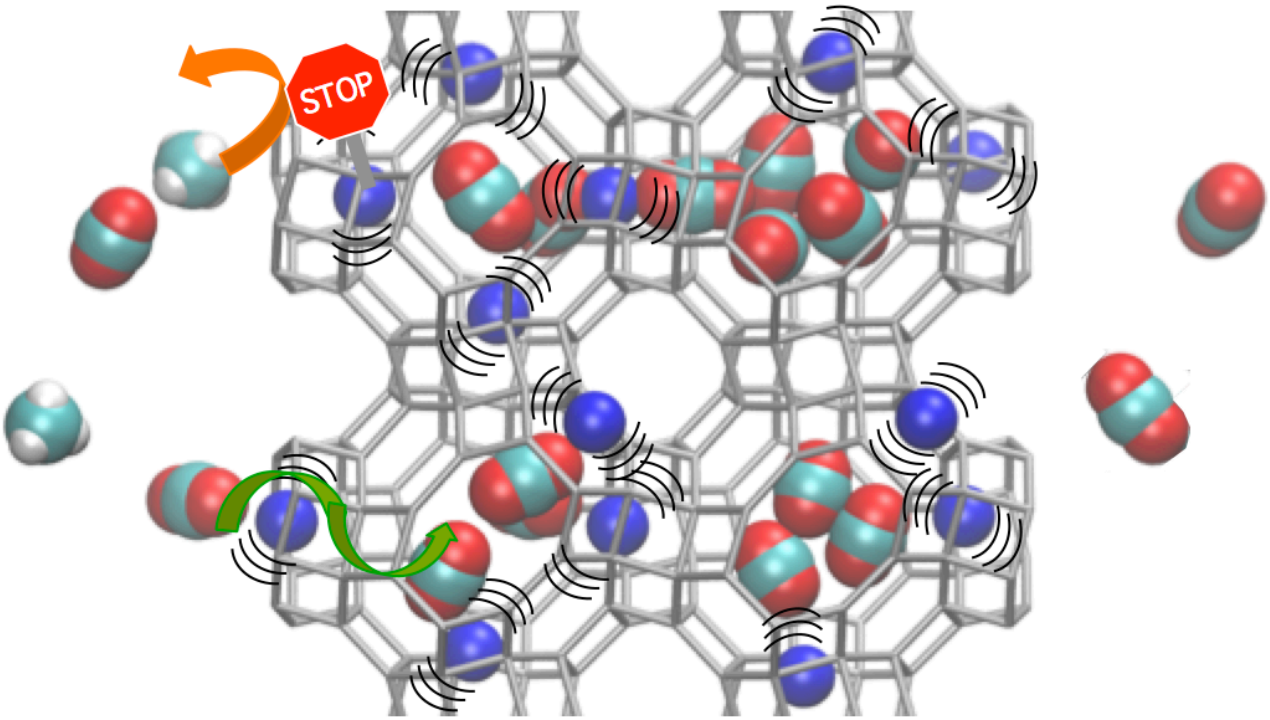
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