

Supporting Information for: Molecular Insight into CO₂ “Trapdoor” Adsorption in Zeolite Na-RHO

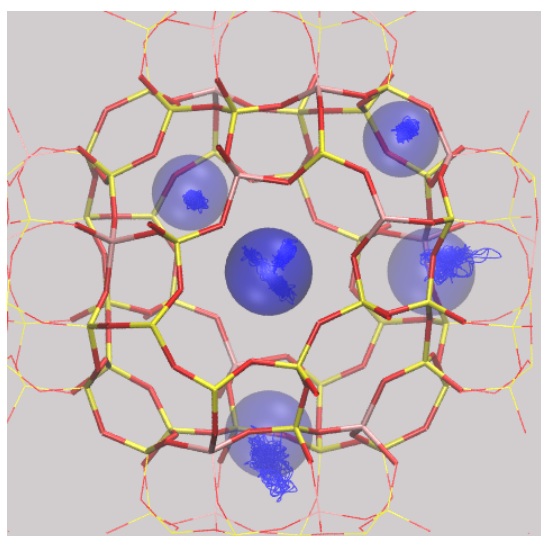
François-Xavier Coudert[†] and Daniela Kohen^{†,‡}

[†] Chimie ParisTech, PSL Research University, CNRS, Institut de Recherche de Chimie Paris, 75005 Paris, France

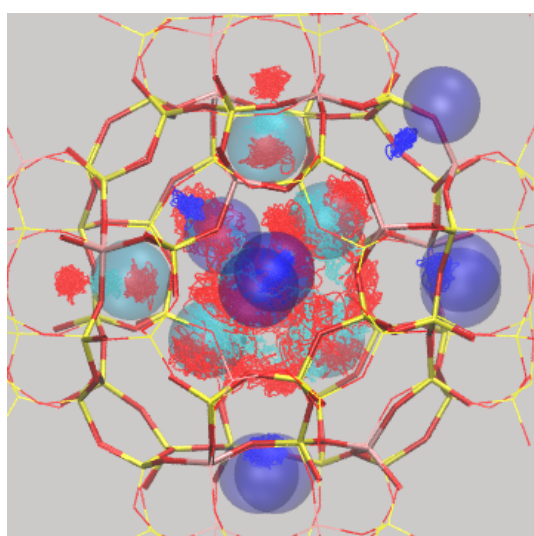
[‡] Department of Chemistry, Carleton College, Northfield, MN 55057, USA

S1: Cation and carbon dioxide locations.

Figure shows the representative trajectories shown in figure 3 of the main text but here transparent balls show the crystallographic positions determined by Lozinska et. al. [*J. Am. Chem. Soc.* **2012**, 134, 17628–17642]. a) Shows the traces of cations in a simulation without adsorbates. Only cations positioned on the central cage shown are displayed as well as the crystallographic sites corresponding to those cations. b) Shows the traces of cations and carbon dioxide molecules in a simulation with 15 molecules of carbon dioxide. Only cations and molecules on the central cage shown are displayed as well as the corresponding crystallographic sites. For clarity only the reported site for the carbon is shown (and not the oxygen atoms even though they were reported). The agreement is pretty good and the biggest difference is on the sitting of the S8R carbon dioxide. Experimentally the C site was not assigned to the center of the S8R, which is puzzling given that the ring exposes 8 oxygen atoms. On the other hand the simulation shows the carbon in the carbon dioxide sitting on the ring.



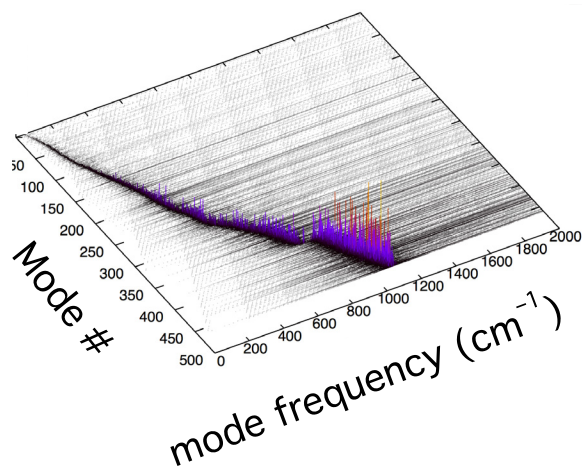
a)



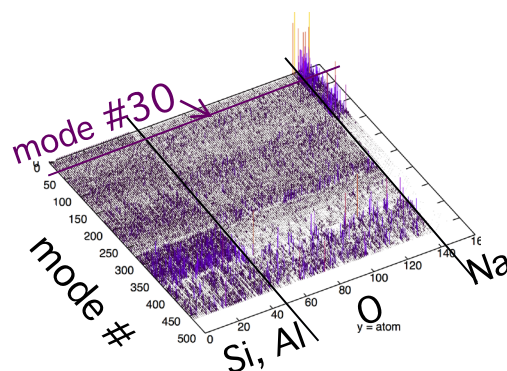
b)

S2: Effective Normal Modes

Na-RHO.



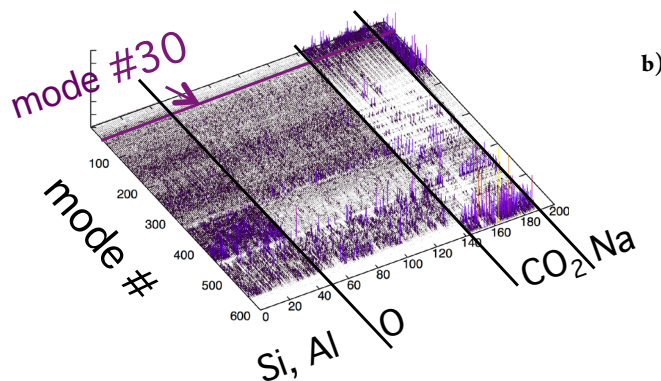
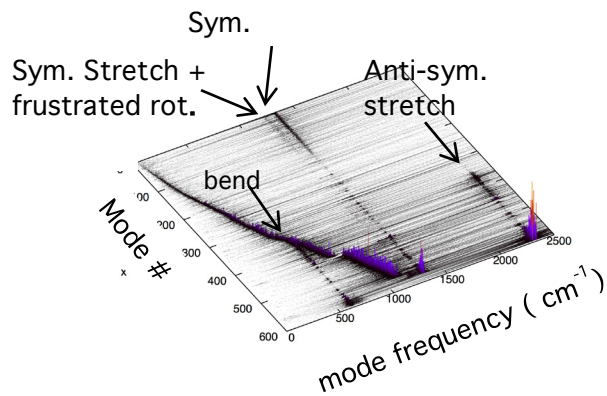
a)



b)

a) Spectra of each of 3 × 154 modes. b) Atoms contributing to each mode. The method allows computing which atoms are involved in each mode revealing the fact that cation motion is involved in more than 120 modes. Given that there are only 10 cations on the system this implies that these modes also have contributions of many other atoms. None of them, however, is really significant as the graph shows.

Na-RHO under 1 atm CO₂.

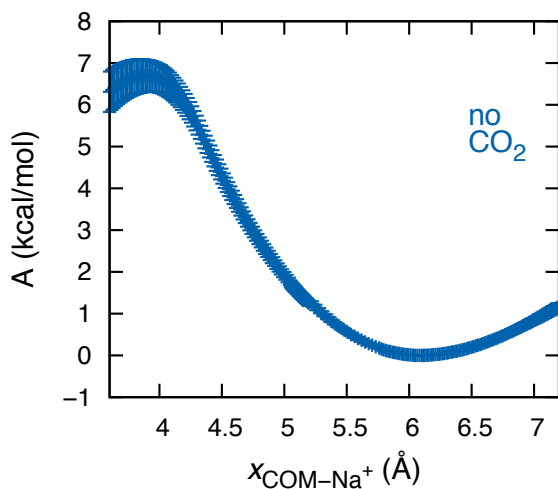


a)

a) Spectra of each of 3×199 modes. Note how in this case the method does not work as well as each mode's spectra is not well isolated and the CO₂ peaks are quite distinguishable. Note that within the effective normal modes method there is an additional step that can be used to correct for molecules that can freely move, as CO₂ are able to. This correction was not applied given that the preliminary results shown here fail to indicate modes of particular interest. b) Atoms contributing to each mode. As when carbon dioxide is absent cation motion is involved in many more than 3×10 modes indicating that these modes also have contributions of many other atoms, including motion from the carbon dioxides as the graph shows.

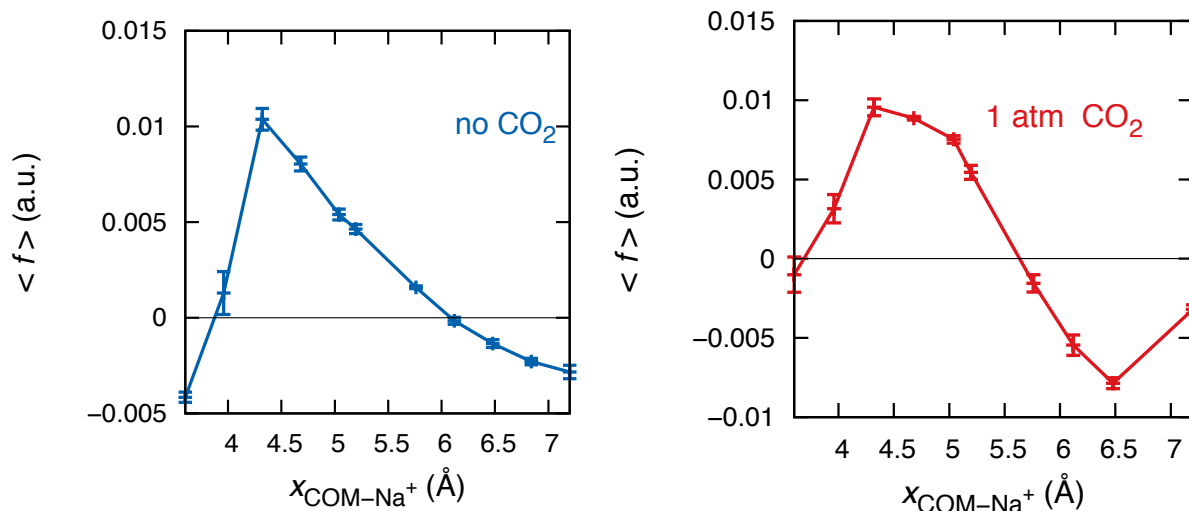
S3. Average forces and free energy profiles

Free energy profile of a cation leaving the blocking S8R site in the absence of carbon dioxide showing errors.

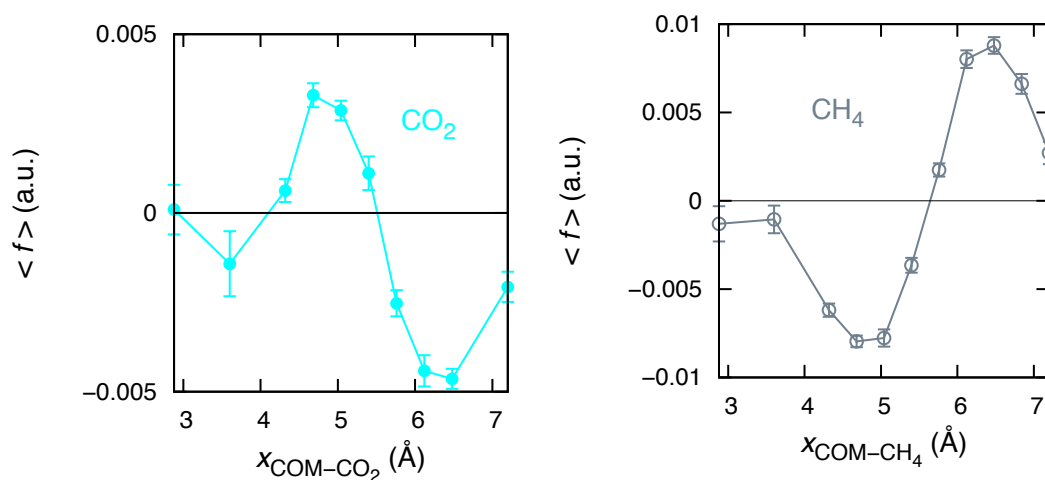


Since the free energy is obtained by integrating over the average force curve the errors accumulate from where the integration starts – in this case around 6.12 Å.

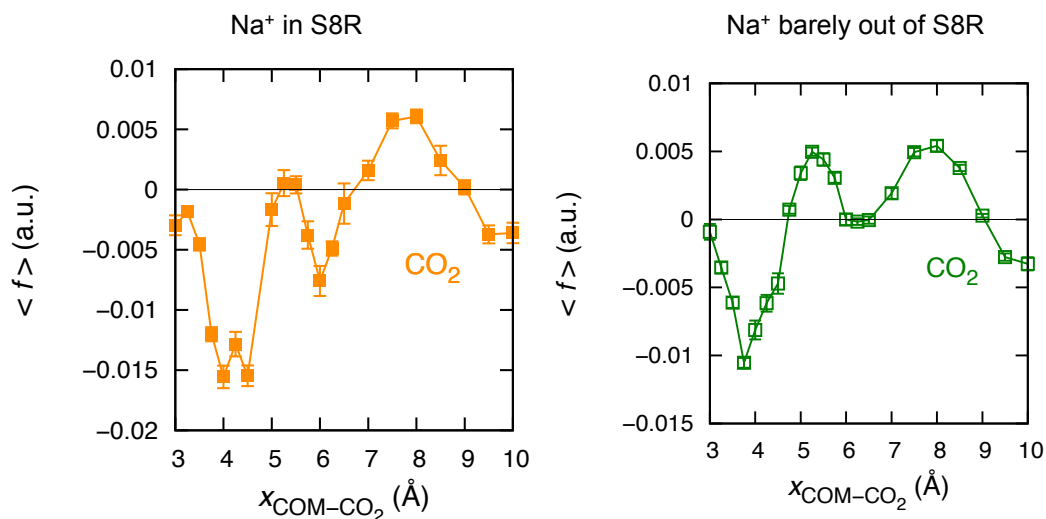
A cation leaving the blocking S8R site in the absence and in the presence of carbon dioxide. Average forces vs. reaction coordinate.



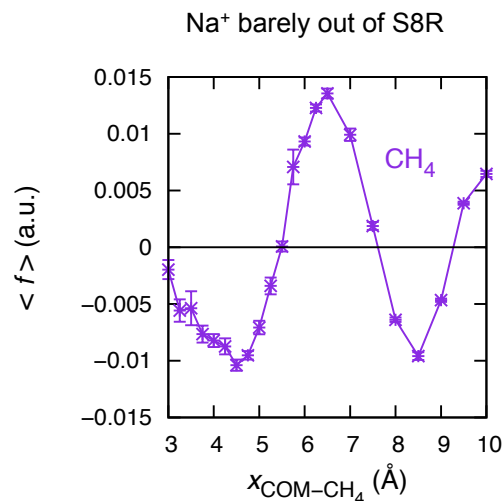
A guest molecule entering a S8R site from the cage. (Unconstrained Cations and none in the narrow pore of interest). Average forces vs. reaction coordinate.



A carbon dioxide molecule entering a S8R site from the cage when a cation is constrained at 5.76 Å and at 4.68 Å. Average forces vs. reaction coordinate.



A methane molecule entering a S8R site from the cage when a cation is constrained at 4.68 Å. Average forces vs. reaction coordinate.



S4. Computational Methods

Initial configurations for the AIMD dynamics.

To find reasonable initial position for the cations, parallel tempering was performed using the RASPA code [Dubbeldam et al, *Mol. Simulat.* **2015**, 42, 81–101] and the classical potential described in the main code. These runs resulted in many double occupied D8R (one cation in each S8R composing the D8R). Five of these configurations were chosen but since Lozinska and collaborators suspect that experimentally most samples have singly occupied D8R two more runs were performed in which all D8R are occupied by only one cation. When necessary, carbon dioxide molecules were introduced after the initial locations for the cations were established.

Initial configurations for the constrained AIMD dynamics.

A cation leaving the blocking S8R site in the absence of carbon dioxide.

All simulations in this series started with the same configuration for all particles but the constrained sodium. The coordinates were taken from one of the AIMD simulations where a cation was sitting on a S8R on the right hand side of the unit cell after 20ps of evolution. There were no cations on the S6R flanking that ring or on the partner S8R (on the left hand side of the unit cell). The series of initial configurations for the constrained cation were obtained by displacing it along the reaction coordinate. This ensured that we were sampling dynamics relevant to a cation leaving its S8R site towards an available neighboring S6R site.

A cation leaving the blocking S8R site in the presence of carbon dioxide.

GCMC were performed to introduce 15 molecules of CO₂ on each member of this series. The initial coordinates of the framework atoms were the crystallographic ones for Na-RHO under 1atm of carbon dioxide, while the initial coordinates of the cations of each member of this series was obtained from the previous series after at least 2 ps of evolution.

A carbon dioxide molecule entering a S8R site from the cage when a cation is constrained at 5.76 Å and at 4.68 Å.

These two series' initial configurations originated on coordinates from the previous series after at least 2 ps of evolution. In each of them the coordinates of the molecule that was to be constrained was generated by displacing its atoms along the x coordinate. The “original” carbon dioxide y and z coordinates were those of one sitting on the S8R on the left hand side of the unit cell to minimize strain when the guest molecule went thru the narrow pore. These initial configurations underwent a quick geometry optimization where the framework and the carbon of the to be constrained CO₂ were kept in place in order to further reduce the strain of the initial configurations. Nevertheless in some cases this procedure still yielded an initial configuration under so much stress that the zeolite broke or the molecule dissociated within fs of starting the constrained AIMD run. To avoid this situation in those cases the initial configurations were modified by hand and then geometry optimized before starting the AIMD run.

A methane molecule entering a S8R site from the cage when a cation is constrained at 4.68 Å.

The procedure here was very similar to the one just described but in this case GCMC was performed to introduce 15 molecules of CH₄ on each member of this series. We wanted to obtain results comparable to those with carbon dioxide but given the lack of affinity of methane for the zeolite this necessitated a large pressure. Also, there is no reliable potential to model methane within Na-RHO so reasonable initial positions were obtained for all-silica RHO using the potential developed by Kaminski et al. [*J. Phys. Chem.* 1994, 98, 13077–13082]

A guest molecule entering a S8R site from the cage. (Unconstrained Cations).

These series initial positions were very similar to corresponding ones in the runs above but the constrained cation was placed “out of the way” on S6R to allow for the sampling of a “totally” open narrow pore.