

Supplementary Data

1. Further details on computations employing empirical potentials

Classical trajectories were calculated with the help of the DL_POLY program.¹ The molecules were treated as rigid, with the help of the SHAKE algorithm.² The calculations employed a 11 Å potential cutoff and Ewald sum for long range electrostatics. Simulation parameters were: time step of 1 fs, SHAKE tolerance of 10^{-8} and Ewald precision of 10^{-10} .

1.1 Potential

Non-polarizable potentials were used, which included Lennard-Jones interactions and Coulomb interaction terms between point charges. For water-water interactions we employed the well known and extensively used TIP4P potential.³ The guests examined computationally included EOX, H₂S and CO₂. The CO₂ parameters were adopted from Harris and Yung (EMP2 potential).⁴ The H₂S parameters were adopted from Vorholtz et al).⁵ Parameters of Lennard Jones interaction between the guests and water were calculated with the usual Lorentz-Bertholet combining rules.⁶ With the present empirical potential for the H₂O..H₂S interaction, the dimer binding energy with H₂S acting as a donor / acceptor is 3.27 / 2.05 kcal/mol; the corresponding values obtained on MP2/aug-cc-pvDz level, with the basis set superposition correction are 2.50 / 2.57 kcal/mol. For EOX, united atom model was used for CH₂. The starting parameters for EOX were adopted from OPLS;⁷ some readjustment was carried out to improve the fit to *ab initio* results for the H₂O..EOX dimer. The final EOX parameters used corresponded to $r_{CO}=1.465$ Å, $\angle COC = 61^\circ$, $\sigma_{oo} = 2.9$ Å, $\epsilon_{oo} = 0.140$ kcal/mol, $\sigma_{cc} = 3.5$ Å, $\epsilon_{cc} = 0.100$ kcal/mol, $q_c = 0.2$, $q_o = -0.1$, $q_m = -0.3$, $r_m = -0.1862$ Å. (The “m-point” denotes the location of most of the negative charge, on the molecular bisector passing through the O-atom, outside the CCO triangle.)

With the present empirical potential for the H₂O..EOX interaction, the dimer binding energy with H₂O acting as a proton donor is 6.8 kcal/mol; the corresponding value obtained on MP2/aug-cc-pvDz level, with the basis set superposition correction, is 5.95 kcal/mol. (However hydrogen bonding to water within condensed phases is in

fact expected to be stronger than bonding in a dimer, due to cooperative effects.) Another discrepancy with respect to *ab initio* is found in the dimer geometry. In MP2 minimum, the EOX plane is nearly perpendicular to the O..O axis, while in the minimum obtained with the empirical potential the angle between the O..O axis and the EOX bisector is close to 160 degrees; still, the potential dependence on this angle is rather flat both for MP2 and for the empirical potential. According to the above potential models, the interactions between the guests and the host lattice are not expected to be very accurate. However, as noted in the article, at the present stage no effort was made to obtain very accurate results for the systems considered. The main objective was to demonstrate qualitative differences between transport in CH with H-bonding guests (EOX, H₂S) versus CH with a guest which cannot engage in significant H-bonding to water (CO₂).

1.2 Calculations of ΔG for defect formation

ΔG values for forming a vacancy and interstitial water were calculated separately, and then combined. ΔG for generating the vacancy / caged water pair was estimated using thermodynamic integration (TI).⁸

$$\Delta G = \int dG = \int_0^1 d\lambda \frac{dG}{d\lambda} = \frac{\langle E(\lambda + \delta\lambda) - E(\lambda) \rangle_\lambda}{\delta\lambda}$$

That is, to calculate ΔG for forming a vacancy, a sequence of systems was imagined in which a water molecule gradually disappears from one of the sites of a simulation cell. The disappearance was described by linear scaling of the Coulombic and van der Waals interactions of that molecule with the rest of the system, by a parameter λ , ranging from 1 to zero. The value of dG was evaluated as an average for $\pm\delta\lambda$ increments of λ , at select λ values, to obtain mapping of $dG/d\lambda$ in the 1-0 λ -range. The values of $d\lambda=0.01$ was used except for the points in the vicinity of $\lambda=0$, where $d\lambda=0.005$ was employed. Thus $\langle E(\lambda + \delta\lambda) \rangle$ and $\langle E(\lambda) \rangle$ in the TI formula above corresponded to configurational potential energy at $\lambda + \delta\lambda$ and λ respectively; the thermal averaging was carried out over a collection of configurations generated by an NVT trajectory corresponding to λ , at the temperature of 130K. The length of the trajectory was 1-2 ns; Berendsen thermostat was used with relaxation constant of 0.5 ps. MD configurations for averaging were collected every 0.3 ps. The

calculated shape of $dG/d\lambda$ is shown in Fig. S1, for vacancy formation in CH with EOX-H₂S guests, and for CH with CO₂ guests.

One well-known difficulty of the above TI procedure for a particle creation in a dense medium, is that a linear TI path results in a divergence at the limit $\lambda = 0$.⁹ In this limit, the integrand is dominated by the repulsive part of the Lennard Jones potential terms, and approaches infinity as $\lambda^{-3/4}$.¹⁰⁻¹² The problem was addressed similarly to ref. 13; the numerical point nearest to the origin ($\lambda = 0.005$) was extrapolated to the origin assuming $\lambda^{-3/4}$ dependence, and the integration variable was transformed to $x = \lambda^{1/4}$; then $\Delta G = \int_0^1 dx (\lambda^{3/4} \frac{dG}{d\lambda})$.

ΔG was finally obtained by numerical integration. The physical system used to evaluate ΔG for vacancy formation corresponded to s-I unit cell, with large cages filled with EOX, and small cages occupied by H₂S. In an additional set of calculations, all guest molecules were replaced by CO₂. The s-I structure host lattice includes three inequivalent water sites.¹⁴ In the calculation of ΔG for vacancy formation, the molecule removed corresponded to “k”-site in Davidson’s notation.¹⁴ Removal of a molecule from this site in the mixed EOX - H₂S CH requires 2 / 8 kcal/mol less energy than H₂O removal from sites “c” and “j”.

The value of ΔG for formation of an interstitial water defect was calculated similarly, by considering gradual emergence of a water molecule in an interstitial position. Insertion of an interstitial into host lattice proved to be somewhat problematic, technically. Finally, we found in numerical tests that placing an extra water molecule into an empty CH cage resulted in insertion of the extra H₂O into the cage wall, and thus to the host lattice. The resulting formation of a traveling interstitial defect was evidenced by diffusion of water within the system. Thus, the model system in this part of the calculation corresponded to one s-I unit cell with seven full cages (6 EOX+1H₂S or 7 CO₂) and one empty cage. The interstitial molecule was identified as a two- or three-coordinated excess molecule inserted into a cage wall; graphic display can be found in the article. To calculate ΔG for removing an interstitial, a sequence of systems was imagined in which a two-coordinated excess

water molecule gradually disappears from the wall of one of the full cages. The TI formula was applied to obtain the corresponding change of free energy; ΔG for forming an interstitial is taken as the same number, with an opposite sign.

Again, as noted above, at the present stage we explored qualitative effects. More quantitative calculation would require a larger physical model and calculation of ΔG values for placing an interstitial or a vacancy at a number of crystal sites.

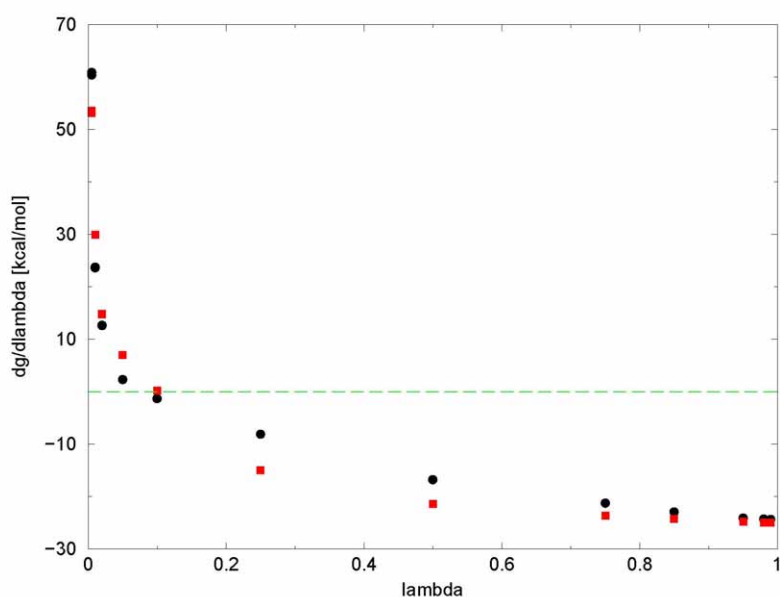


Fig. S1: The calculated values of $dG/d\lambda$ for vacancy formation in the EOX/H₂S CH (circles) and CO₂ CH (squares). The statistical uncertainty of the averages is in the range of 0.6-0.01 kcal/mol where the highest uncertainty pertains to the lowest λ value of 0.005. The points obtained for $\pm\delta\lambda$ increments overlap in the figure, differing at most by 0.4 kcal/mol at the low end of the plot, but typically agreeing within better than 0.1 kcal/mol. The shape of the plots for the disappearance of the interstitials as well as the corresponding statistical uncertainties are qualitatively similar.

1.3 Computational studies of molecular diffusion in CH

Studies of molecular diffusion were carried out for various cage occupancies using a model with a single s-I unit cell and either a vacancy or an interstitial defect in the host lattice. The aim was a rough estimate of molecular mobilities, and of the corresponding activation barriers. NVE simulations lasting ~ 10 ns were used, at several mean temperatures in the 210-250 K range. Below, examples of calculated mean square displacements (m.s.d.) are shown, for a system with 6 guests in the large cell, and a single guest in a small cell. (As explained above, this system was found convenient for introducing an interstitial defect into the CH.)

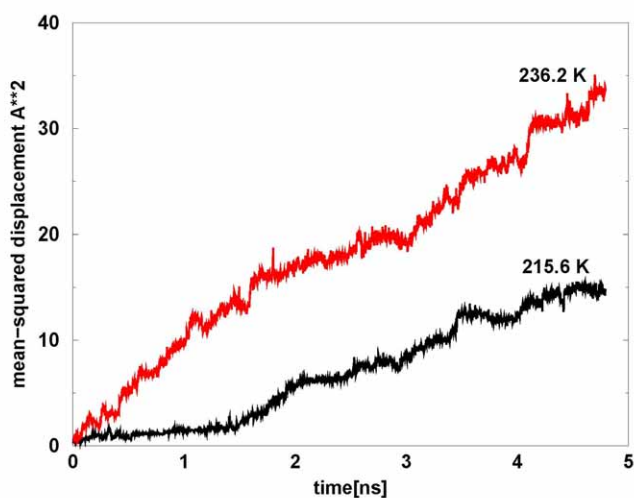


Fig. S2 Mean squared displacement of H₂O in a simulation box with a single interstitial defect within an s-I unit cell. From NVE runs at two different average temperatures. The model includes six EOX guests and one H₂S guest. Assuming exponential dependence of the diffusion rate, activation barrier of ~4.3 kcal/mol is estimated.

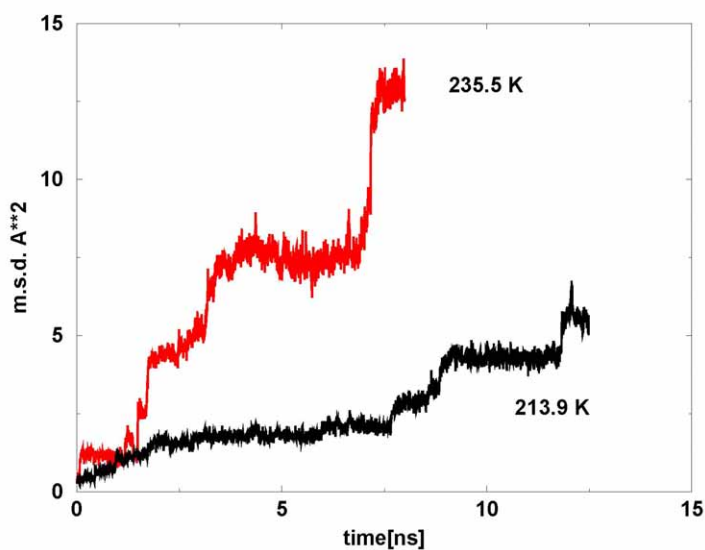


Fig. S3 Mean squared displacement of H₂O in a simulation box with a single vacancy within an s-I unit cell. From NVE runs at two different average temperatures. The model includes six EOX guests and one H₂S guest. Assuming exponential dependence of the diffusion rate, activation barrier of ~5.0 kcal/mol is estimated.

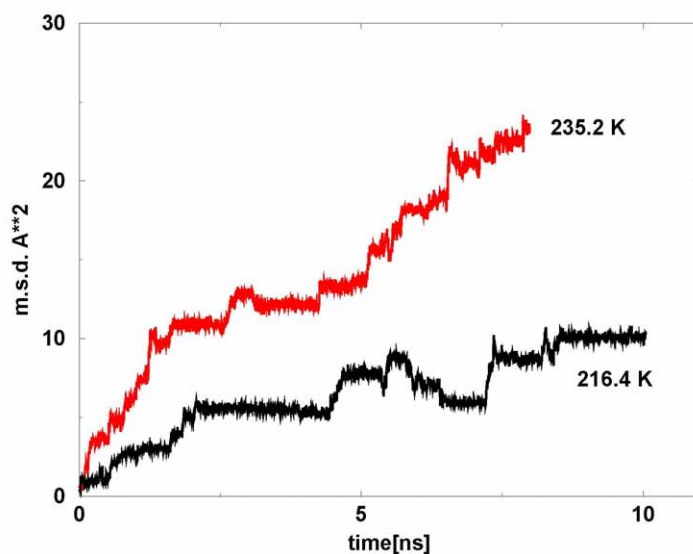


Fig. S4 Mean squared displacement of H₂O in a simulation box with a single interstitial defect within an s-I unit cell. From NVE runs at two different average temperatures. The model includes seven CO₂ guests. Assuming exponential dependence of the diffusion rate, activation barrier of ~5.1 kcal/mol is estimated.

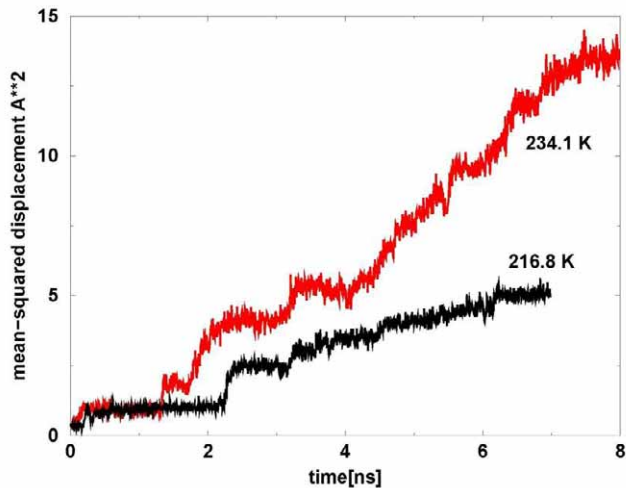


Fig. S5 Mean squared displacement of H₂O in a simulation box with a single vacancy within an s-I unit cell. From NVE runs at two different average temperatures. The model includes seven CO₂ guests. Assuming exponential dependence of the diffusion rate, activation barrier of ~4.9 kcal/mol is estimated.

To observe significant guest hopping in an S-I unit cell, we had to include two empty cages into the model. In the runs used to derive mean squared displacements

below, the initial configuration included five guest molecules in the large cage and one guest molecule in the small cage.

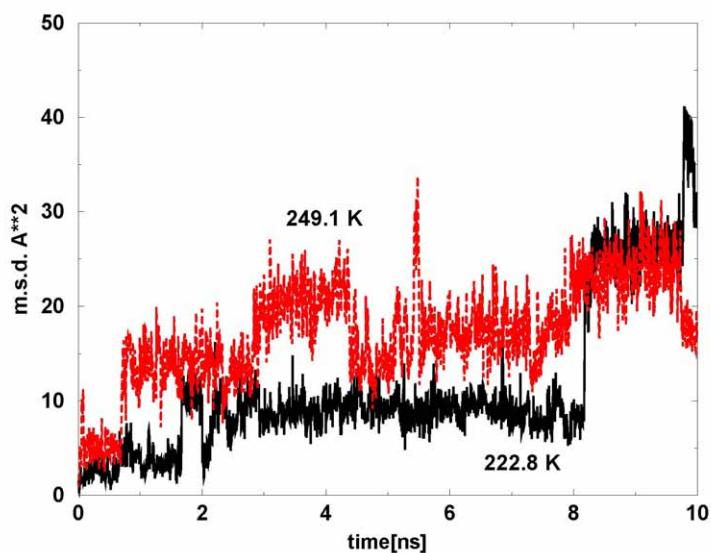


Fig. S6. Mean squared displacement of guest molecules in a simulation box with a single vacancy within an s-I unit cell. From NVE runs at two different average temperatures. The model includes five EOX guests and one H₂S guest. Hopping of both guests was observed and contributes to the plot.

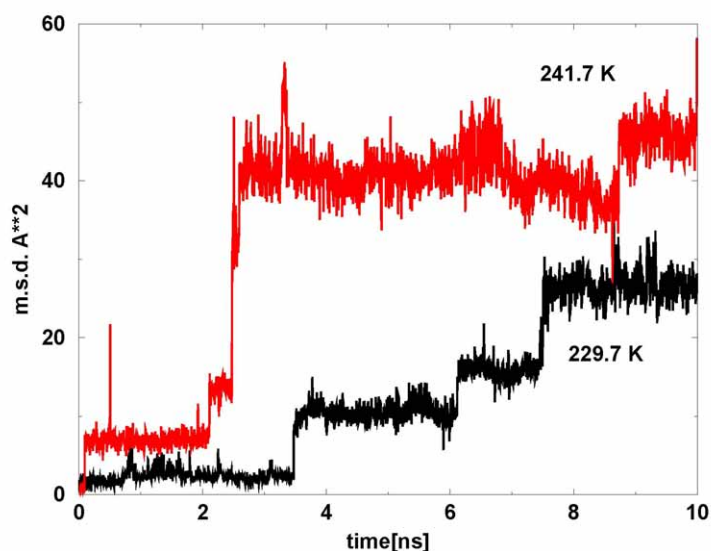


Fig. S7. Mean squared displacement of CO₂ in a simulation box with a single vacancy within an s-I unit cell. From NVE runs at two different average temperatures. The model includes six CO₂ guests.

2. References: Supplementary Data

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