



Supporting Information

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# Hydrogen Gas Migration through Clathrate Hydrate Cages

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## Molecular Dynamics Calculations

The force field used for the clathrates is similar to that used in our previous simulations on H<sub>2</sub> clathrate hydrates.<sup>[1]</sup> Water molecules in the simulations are modeled by the extended simple point charge (SPC/E) model.<sup>[2]</sup> The hydrogen molecule is considered rigid, with a bond length of 0.7414 Å which corresponds to the experimental gas-phase value.<sup>[3]</sup> To reproduce the experimental gas-phase quadrupole moment of H<sub>2</sub> of  $2.172 \times 10^{-40} \text{ C}\cdot\text{m}^2$ ,<sup>[4]</sup> point charges are placed at the hydrogen nuclei and at the centre of mass of the hydrogen molecule. An isotropic Lennard-Jones potential based on the well depth and potential minimum of the Silvera - Goldman isotropic pair potential for gas-phase hydrogen<sup>[5]</sup> is used to describe the H<sub>2</sub>-H<sub>2</sub> interactions.

Intermolecular potentials taken as the sum of Lennard-Jones 12-6 centered on the hydrogen center of mass and electrostatic point charge potentials centered on the hydrogen atoms and hydrogen molecule center of mass,

$$V(\text{inter}) = \sum_{i=1}^{N-1} \sum_{j>i}^N \left\{ 4\varepsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \right\}. \quad (1)$$

Point charges  $q_i$  and  $q_j$  located on the atomic nuclei  $i$  and  $j$  on different molecules are used to model electrostatic intermolecular interactions. Lorentz-Bertholet combination rules,  $\varepsilon_{ij} = (\varepsilon_{ii} \varepsilon_{jj})^{1/2}$  and  $\sigma_{ij} = (\sigma_{ii} \sigma_{jj})^{1/2}$ , were used for the Lennard-Jones potential

parameters between unlike force centers  $i$  and  $j$ . The values of the intermolecular potential parameters are given in Table I.

**TABLE S1.** Atomic charges and Lennard-Jones interaction parameters for SPC/E water and the rigid H<sub>2</sub> molecule used in the MD simulations.

Atom	$q$ ( $e$ )	$\sigma_{ii}$ ( $\text{\AA}$ ) <sup>a</sup>	$\varepsilon_{ii}$ (kJ/mol) <sup>a</sup>
O (water)	-0.8476	3.166	0.6502
H (water)	+0.4238	0.000	0.0000
H (guest)	+0.4932	0.000	0.0000
HCM (guest) <sup>b</sup>	-0.9864	3.038	0.2852

<sup>a</sup> The intermolecular potential parameters between unlike atoms are determined from Lorentz-Bertholet combination rules.

<sup>b</sup> Corresponds to the center of mass of the H<sub>2</sub> molecule.

Isotropic NVE molecular dynamics simulations were performed on a periodic 2×2×2 (33.96 Å per side) sII clathrate hydrate cubic supercell with the DL\_POLY version 2.14 molecular dynamics package.<sup>[6]</sup> The simulation placed one hydrogen guest in each of the small and large cages. The initial configuration for the simulation was from an equilibrated simulation at 100 K and ambient pressure. The equations of motion were integrated with a time step of 1 fs using the Verlet leapfrog algorithm.<sup>[7],[8]</sup> Long-range electrostatic interactions were calculated using the Ewald summation method<sup>[7],[8]</sup> with a precision of  $1 \times 10^{-6}$  and all intermolecular interactions in the simulation box were calculated within a cutoff distance of  $R_{cutoff} = 15.0$  Å.

## Results

*a) Rattling vibration frequencies of hydrogen guests in the small and large cages*

The reduced velocity autocorrelation functions (VACF),  $\langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle / \langle \mathbf{v}(0) \cdot \mathbf{v}(0) \rangle$ , for the motion of the hydrogen center of mass in the large and small sII cages calculated from molecular dynamics calculations at 100 K and 1 bar were calculated from the NVE MD simulations and the results are shown in the bottom panels of Figures S1 and S2, respectively. Similar calculations have also been performed for 150 K and 2 kbar and the results for the VACF are shown in Figs. S3 and S4.

Fast Fourier Transform of the VACF is used to calculate the rattling vibration frequency and period of the guest motion. The hydrogen guest motions in the large and small cages have frequency distributions with a peak at 1.5 and 3.0 THz, respectively, at 100 K and 1 bar. At 150 K and 2 kbar, the rattling frequencies show a small increase to  $\sim$  2 THz and 3.5 THz in the large and small cages, respectively. The rattling frequency which is considered to be equivalent to the Arrhenius *A*-factor is seen to have a small temperature and pressure dependence.

*b) Kinetics calculations*

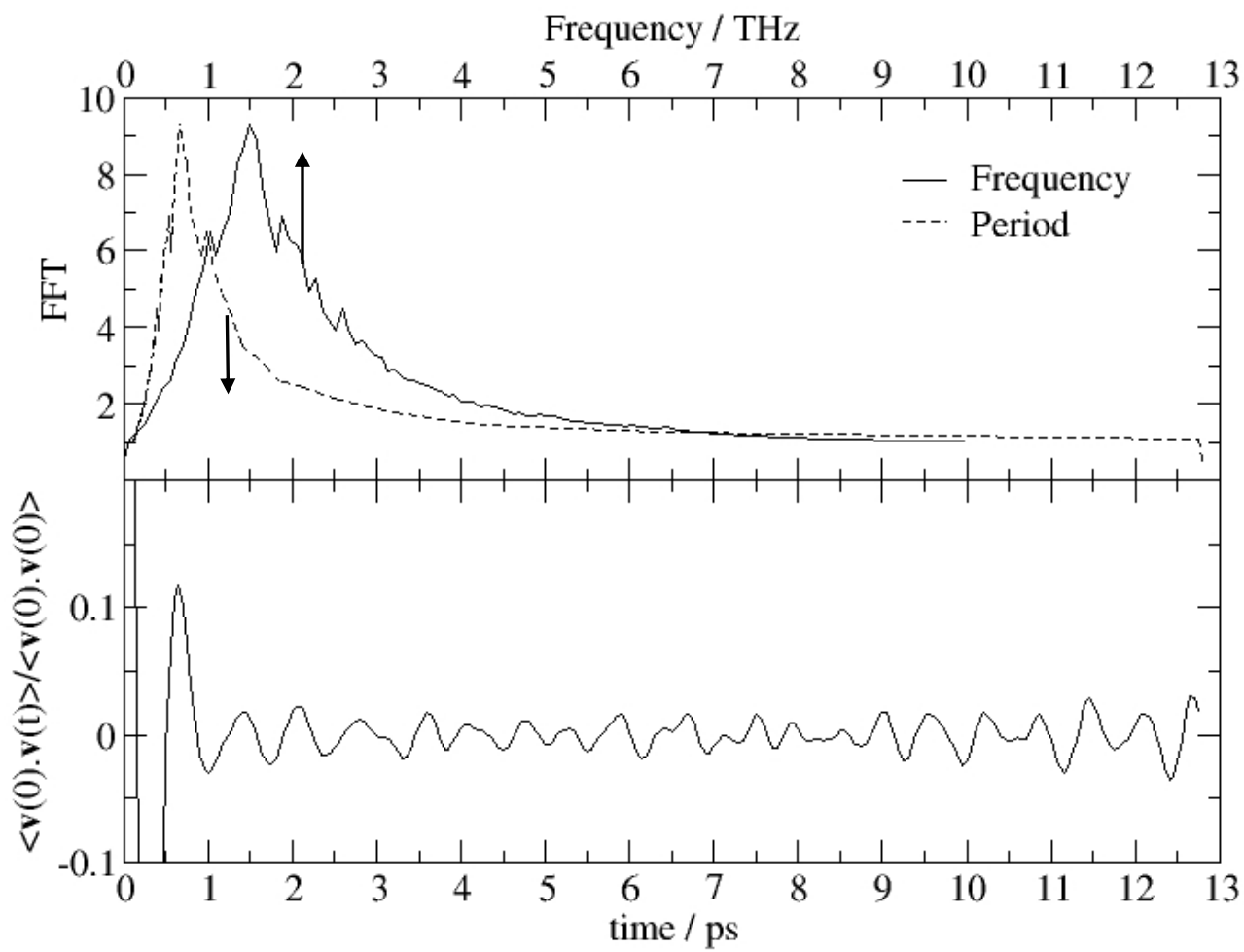
The temperature dependence of the tunneling correction is given by Eq. (4) of the manuscript. Using the tunneling parameters given in Table 1 of the manuscript, the tunneling corrections shown in Fig. S5 are calculated. The tunneling contributions are large at low temperature. For example for the small cage hydrogen tunneling, the tunneling correction is roughly 3. At the high temperature limit where hydrogen migration rates start to increase, the tunneling corrections reduce to unity.

The Arrhenius plot for the temperature dependence of the rates of migration and the self-diffusion coefficients are shown in Fig. S6. At the high temperatures of interest, the deviations from the linear Arrhenius plots are negligible.

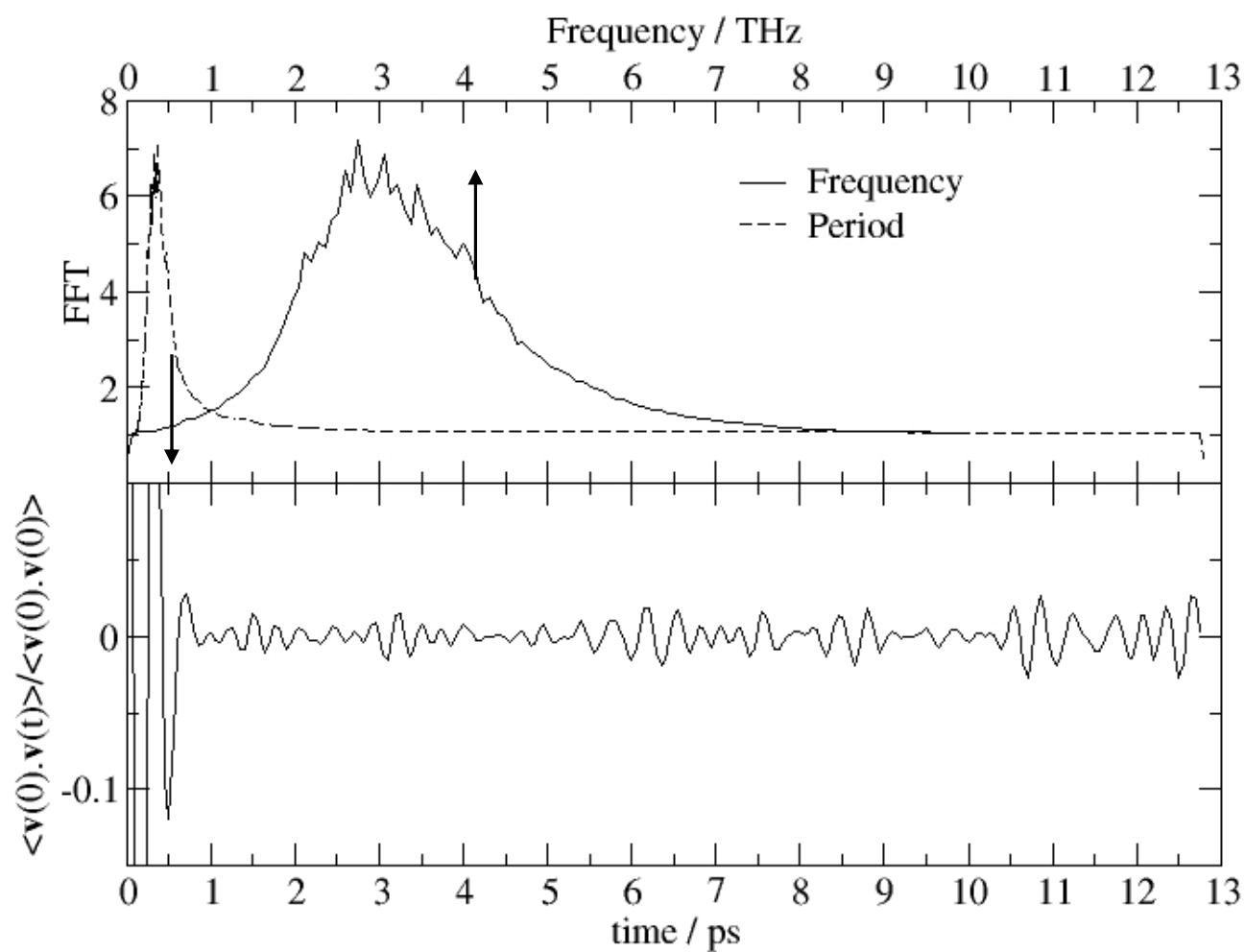
## References

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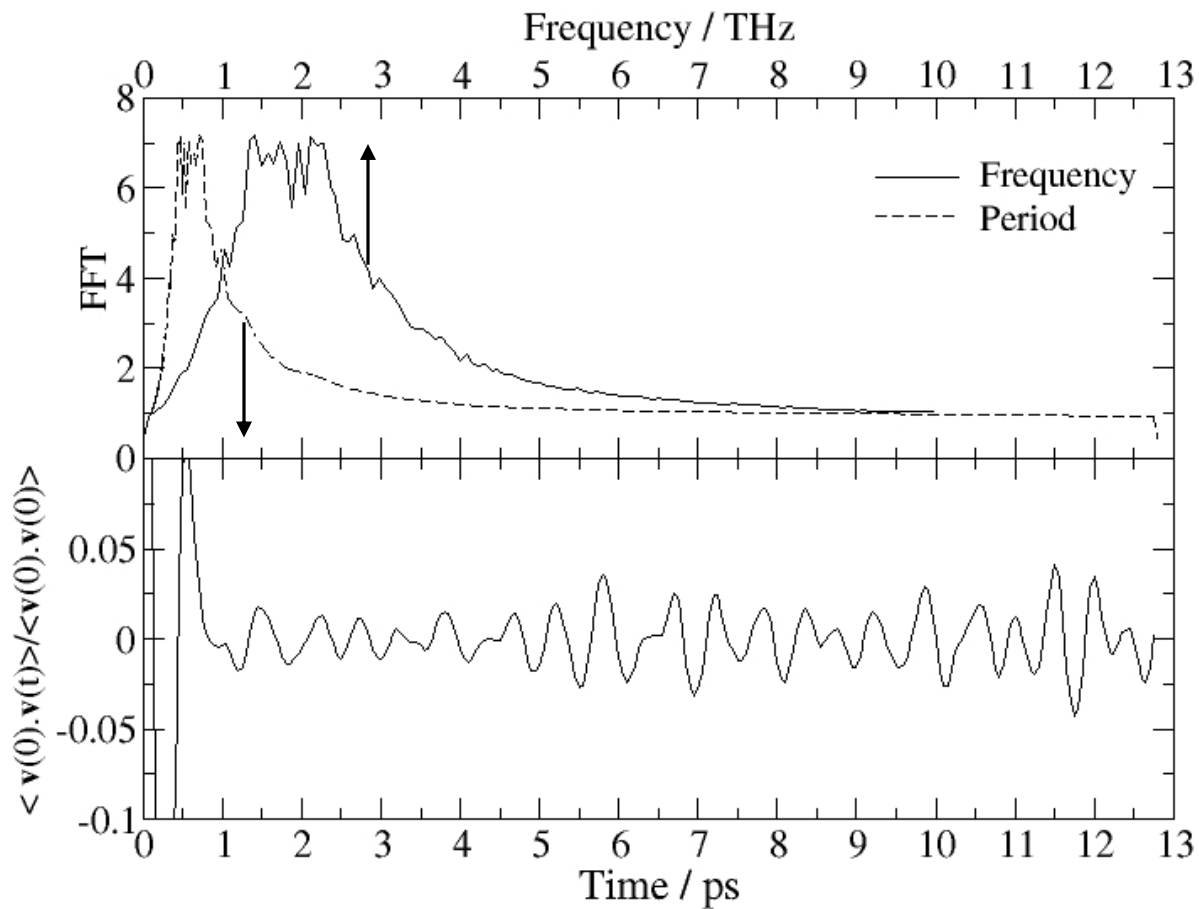
## Figures



**Figure S1.** The velocity autocorrelation function for the motion of the hydrogen centre-of-mass in the large sII cages calculated from molecular dynamics calculations at 100 K and 1 bar (lower panel). Fast Fourier Transform of the VACF was used to calculate the vibrational frequency and period of the guest motion (upper panel). The hydrogen guest motion in the large cage has a frequency distribution with a peak at  $\sim 1.5$  THz.

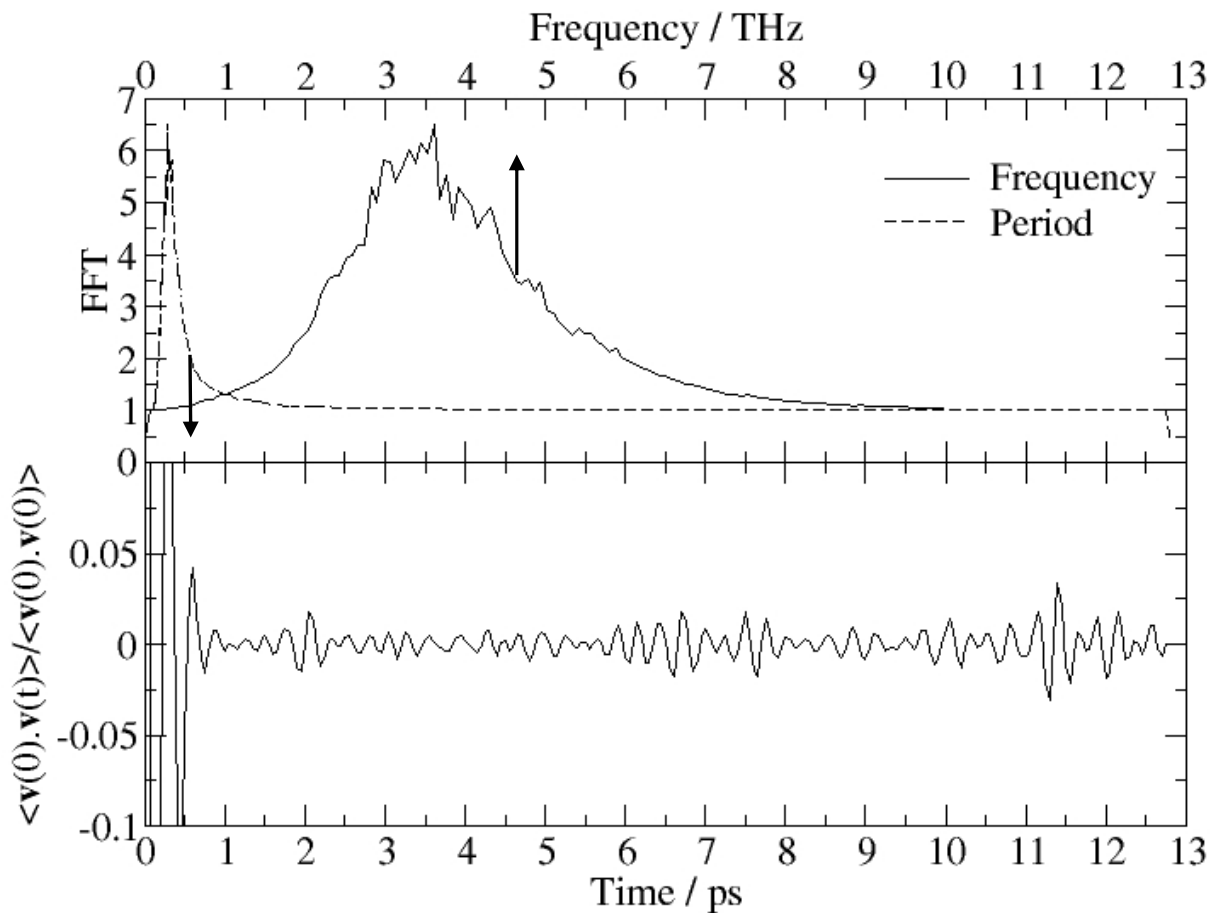


**Figure S2.** The velocity autocorrelation function for the motion of the hydrogen centre-of-mass in the small sII cages calculated from molecular dynamics calculations at 100 K and 1 bar. Fast Fourier Transform of the VACF determines that the hydrogen guest motion in the small cages has a frequency distribution with a peak at  $\sim 3$  THz.

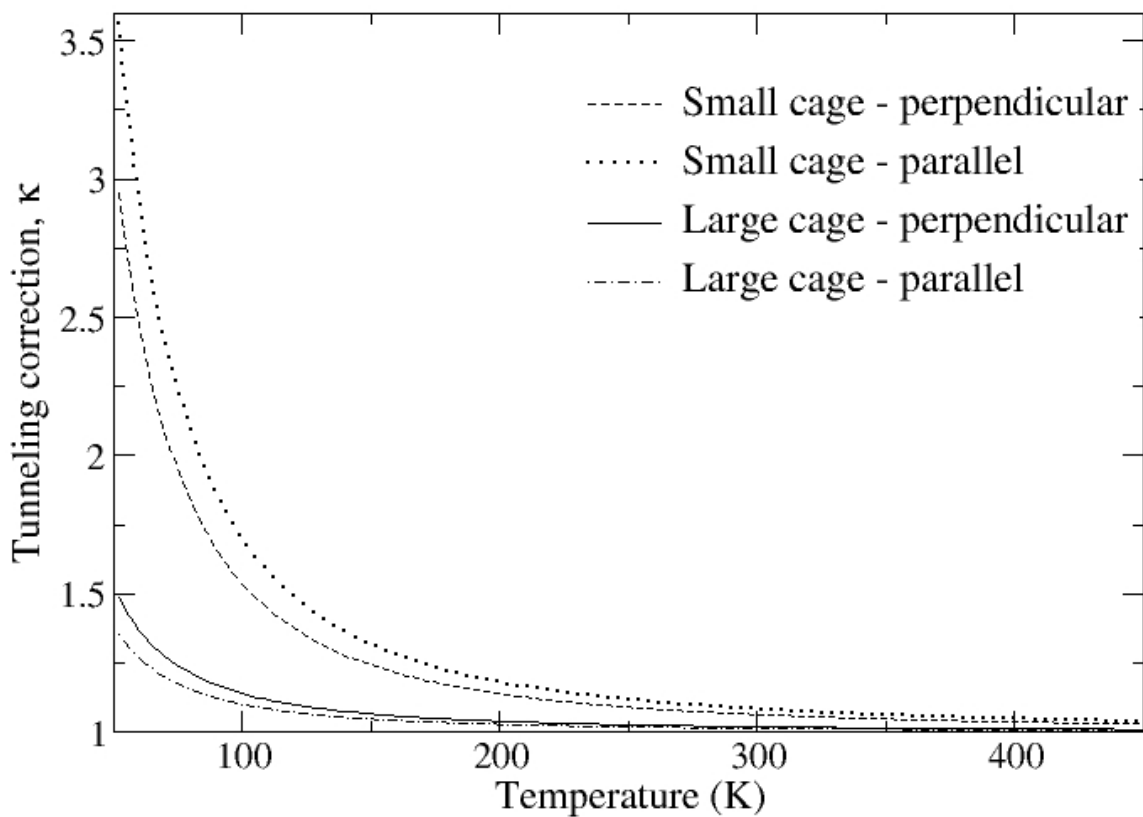


**Figure S3.** The velocity autocorrelation function for the motion of the hydrogen centre-of-mass in the large sII cages calculated from molecular dynamics calculations at 150 K and 2 kbar (lower panel). Fast Fourier Transform of the VACF was used to calculate the vibrational frequency and period of the guest motion (upper panel). The hydrogen guest motion in the large cage has a frequency distribution with a peak at  $\sim 2$  THz.

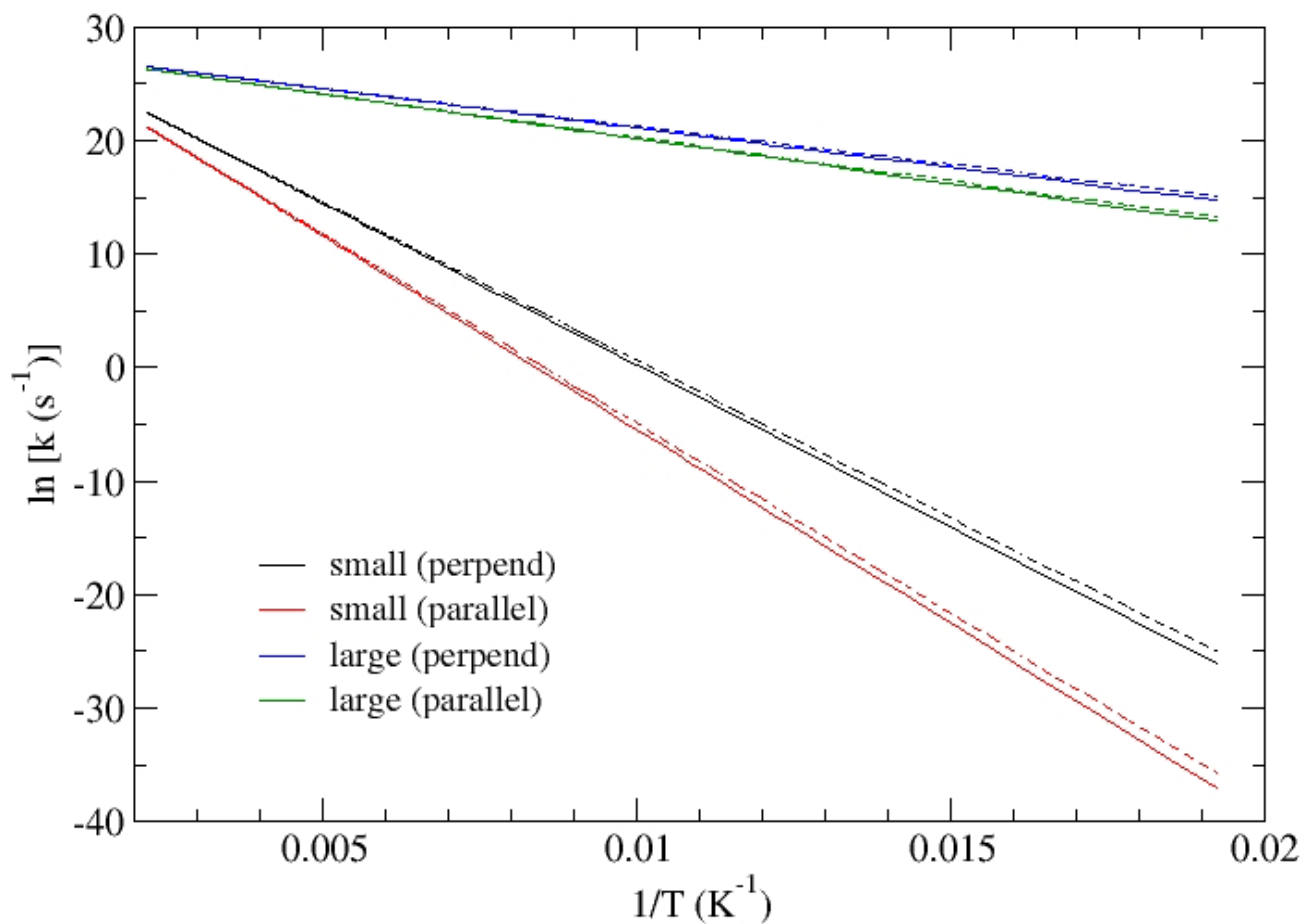




**Figure S4.** The velocity autocorrelation function for the motion of the hydrogen centre-of-mass in the small sII cages calculated from molecular dynamics calculations at 150 K and 2 kbar. Fast Fourier Transform of the VACF determines that the hydrogen guest motion in the small cages has a frequency distribution with a peak at  $\sim 3.5$  THz.



**Figure S5.** The temperature dependence of the tunneling correction for the hydrogen migration through the small and large sII cages. The contribution of tunneling to the migration of hydrogen from the small cages can be substantial at low temperatures.



**Figure S6.** The Arrhenius plot for the rate of hydrogen migration through the small and large sII cages. The rates without tunneling contributions are shown with solid lines and the rates with the tunneling contribution are shown with dashed lines.