Molecular mobility in carbon dioxide hydrates

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Equilibrium lattice constant

Table S1. Equilibrium lattice constant, Å, for the different cases described in the article

T (K)	Case 1	Case 2	Case 3	Case 4	Case 5	Case 6
280	-	-	11.939	11.936	-	-
285	-	11.948	11.944	11.942	-	11.952
290	11.957	11.954	11.949	11.947	-	11.957
295	11.962	11.959	11.954	11.953	-	11.962
300	11.967	11.965	11.958	11.957	11.968	11.967
305	11.972	11.969	11.965	11.962	11.972	11.971
310	11.975	11.974	-	-	11.977	-
315	-	-	-	-	11.983	-

Calculation of free energy barrier for carbon dioxide diffusion

Table S2. Number of carbon dioxide molecule jumps, N, and hopping rate, k, for the different cases described in the article, where "-" denotes no simulation conducted, "*" denotes no jumps were observed during the simulation time, and "--" denotes a melted case.

	Case 1			Case 2		Case 3		Case 4		Case 5		Case 6	
T (K)		N	k (×10^8 s^{-1})	N	k (×10^8 s^{-1})	N	k (×10^8 s^{-1})	N	k (×10^8 s^{-1})	N	k (×10^8 s^{-1})	N	k (×10^8 s^{-1})
280		-	-	-	-	42	4.2	91	9.1	-	-	-	-
285		-	-	2	0.2	52	5.2	95	9.5	-	-	1	0.1
290		*	*	7	0.7	34	3.4	112	11.2	*	*	1	0.1
295		*	*	4	0.4	34	3.4	98	9.8	*	*	3	0.3
300	Run1 Run2 Run3	5 5 5	0.5 0.5 0.5	7	0.7	54	5.4	154	15.4	1	0.1	2	0.2
305	Run1 Run2 Run3	2 2 6	0.2 0.2 0.6	30	3.0	60	6.0	187	18.7	1	0.1	10	1.0
310	Run1 Run2 Run3	25 29 30	2.5 2.9 3.0	31	3.1	--	--	--	--	4	0.4	--	--
315		--	--	--	--	-	-	-	-	22	2.2	--	--

This data was used in the fitting of the linear form of the Transition State Theory (TST) equation:

$$\ln\frac{k}{T} = -\frac{\Delta H}{k_B}\frac{1}{T} + \ln\frac{k_B}{h} + \frac{\Delta S}{k_B} \qquad (1)$$

The notation has been described in the main text. Linear regression was used to calculate the enthalpy and entropy of activation in every case with 1K n data points as follows[1]:

$$\theta = \left(X^T W X\right)^{-1} X^T W Y \qquad (2)$$

where $\theta = \begin{pmatrix} \ln\frac{k_B}{h} + \frac{\Delta S}{k_B} \\ -\frac{\Delta H}{k_B} \end{pmatrix}$, $X = \begin{pmatrix} 1 & 1/T_1 \\ \text{M} & \text{M} \\ 1 & 1/T_n \end{pmatrix}$, $Y = \begin{pmatrix} \ln\left(k_1/T_1\right) \\ \text{M} \\ \ln\left(k_n/T_n\right) \end{pmatrix}$,

$$W = \begin{pmatrix} N_1 \Big/ \sum_{i=1}^{n} N_i & 0 & \text{L} & 0 \\ 0 & \text{O} & & \text{M} \\ \text{M} & & \text{O} & 0 \\ 0 & \text{L} & 0 & N_n \Big/ \sum_{i=1}^{n} N_i \end{pmatrix}$$

Depictions of the different hopping scenarios

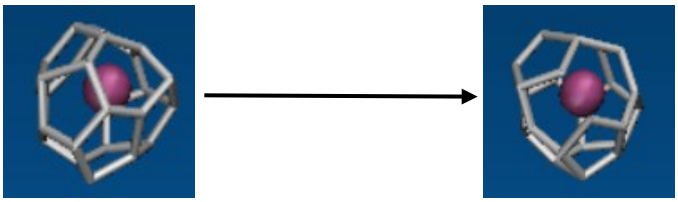

Figure S1: Large cage ($5^{12}6^2$) transition just before large to large cage hopping takes place through the hexagonal face. The hydrogen bonding is represented with grey sticks for water molecules that are within 3.3 Å of each other. The carbon dioxide molecules are represented with the purple sphere.

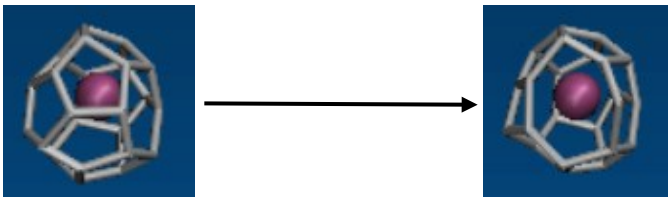

Figure S2: Large cage ($5^{12}6^2$) transition just before large to large cage hopping takes place through the pentagonal face. The color representations are as in Figure S1.

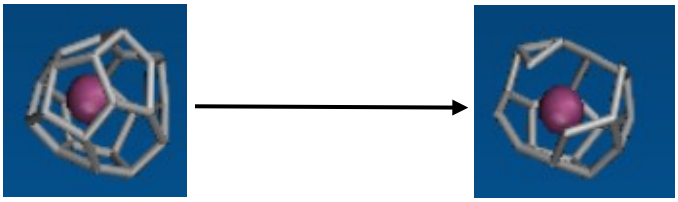

Figure S3: Large cage ($5^{12}6^2$) transition just before large to small (5^{12}) cage hopping takes place. The color representations are as in Figure S1.

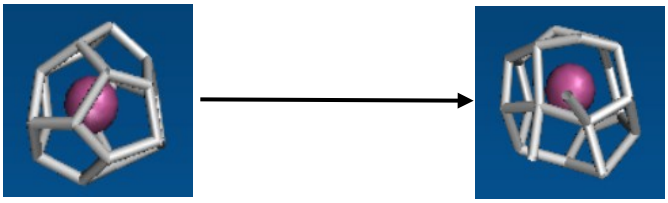

Figure S4: Small cage (5^{12}) transition just before small to large ($5^{12}6^2$) cage hopping takes place. The color representations are as in Figure S1.

A parameter fitting results for carbon dioxide diffusion

Table S3. *A* parameter fitting results for carbon dioxide diffusion

T (K)	Case 1	Case 2	Case 3	Case 4	Case 5	Case 6
280	-	-	0.0030	0.0083	-	-
285	-	0.0010	0.059	0.00067	-	0.020
290	-	0.0038	0.0016	0.00056	-	0.041
295	-	0.00054	0.0018	0.0024	-	0.0013
300	0.050	0.00034	0.00060	0.00063	0.14	0.0058
305	0.0023	-	0.0083	0.00090	0.019	0.0054
310	0.0026	0.0041	-	-	0.0040	-
315	-	-	-	-	0.0099	-

Diffusion coefficients fitting results

Table S4. D_{CO_2} and D_{H_2O} fitting results in 10^{-15} $m^2 \cdot s^{-1}$ and 10^{-13} $m^2 \cdot s^{-1}$, respectively.

T (K)	Case 1		Case 2		Case 3		Case 4		Case 5		Case 6	
	D_{CO_2}	D_{H_2O}	D_{CO_2}	D_{H_2O}	D_{CO_2}	D_{H_2O}	D_{CO_2}	D_{H_2O}	D_{CO_2}	D_{H_2O}	D_{CO_2}	D_{H_2O}
280	-	-	-	-	6.4	2.3	48	3.0	-	-	-	-
285	-	-	4.1	1.4	17	2.6	22	4.0	-	-	3.1	0.14
290	-	-	4.2	1.7	23	4.1	47	4.7	-	-	5.5	0.36
295	-	-	9.6	2.2	3.8	5.6	88	6.7	-	-	5.3	0.77
300	0.18	2.2	3.4	3.5	41	6.6	99	10	0.22	1.3	3.8	0.86
305	2.0	2.2	-	5.3	57	9.5	141	12	0.24	1.6	11	2.6
310	16	7.5	23	8.9	-	-	-	-	3.7	5.3	-	-
315	-	-	-	-	-	-	-	-	17	12	-	-

References

(1) S. Liang, D. Liang, N. Wu, L. Yi and G. Hu, *J. Phys. Chem. C*, 2016, **120**, 16298–16304.