# Supplementary material

for

# **Resolving the Organization of CO<sub>2</sub> Molecules Confined in Silica** Nanopores Using *In-Situ* Small-Angle Neutron Scattering and Molecular Dynamics Simulations

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#### S1. The optimization of β-cristobalite silica unit cell using Density Functional Theory

The convergence of total energy as a function of the kinetic energy cutoff of wavefunctions and K-points mesh is shown in **Figure S1**. The coordinates of the initial and optimized cells are listed in **Table S1**. The optimized cell coordinates have been used to generate silica surfaces and cleave MCM-41 and SBA-15 pores in the prepared surfaces.



**Figure S1.** The total energy convergence as a function of the kinetic energy of the wavefunctions (top) and the k-points mesh (bottom). The inset shows the initial configuration of the silica unitcell.

	Initial coordinates			Optimized coordinates		
Atom	X	Y	Z	X	Y	Z
0	1.193525	0.513929	1.239801	1.174581109	0.617085557	1.309141220
0	3.784475	4.464071	4.713801	3.803418891	4.360914443	4.783141220
0	1.975071	3.682525	2.976801	1.871914443	3.663581109	3.046141220
Ο	3.002929	1.295475	6.450801	3.106085557	1.314418891	6.520141220
0	1.295475	3.002929	0.497199	1.314418891	3.106085557	0.427858780
0	3.682525	1.975071	3.971199	3.663581109	1.871914443	3.901858780
0	0.513929	1.193525	5.708199	0.617085557	1.174581109	5.638858780
0	4.464071	3.784475	2.234199	4.360914443	3.803418891	2.164858780
Si	1.493599	1.493599	0.000000	1.538518630	1.538518630	0.000000000
Si	3.484401	3.484401	3.474000	3.439481370	3.439481370	3.474000000
Si	0.995401	3.982599	1.737000	0.950481370	4.027518630	1.737000000
Si	3.982599	0.995401	5.211000	4.027518630	0.950481370	5.211000000

Table S1. The initial and optimized coordinates of the silica unit cell.

## S2. The core-shell structure of confined CO<sub>2</sub>

The governed shell thickness from small angle neutron scattering and molecular dynamics simulations are listed in **Table S2**. The absolute difference (/D/) between the thickness value obtained by SANS and MD are calculated as follows:

$$\left|D\right| = \left|\frac{SANS - MD}{SANS}\right| \times 100$$

**Table S2.** The values of the shell thickness of  $CO_2$  on MCM-41 and SBA-15 pore surfaces as a function of the pressure.

MCM-41				SBA-15			
Pressure (bar)	SANS	MD	Absolute difference (%)	Pressure (bar)	SANS	MD	Absolute difference (%)
0.000	0	0	0	0.000	0	0	0.00
0.980	$0.74\pm0.05$	$0.56\pm0.03$	23.68	0.930	$2.16\pm0.04$	$1.95\pm0.05$	9.72
14.92	$2.17\pm0.03$	$1.71\pm0.04$	21.19	15.39	$2.87\pm0.02$	$2.60\pm0.02$	9.41
24.88	$2.23\pm0.05$	$1.96\pm0.04$	12.11	24.95	$5.09\pm0.03$	$4.92\pm0.03$	3.34
34.72	$6.73\pm0.05$	$6.15\pm0.05$	8.62	34.91	$8.76\pm0.04$	$8.26\pm0.03$	5.71
44.89	$11.48 \pm 0.03$	$10.09 \pm 0.02$	12.11	44.98	$12.41 \pm 0.04$	$13.75 \pm 0.04$	10.80
54.89	$12.62 \pm 0.06$	$11.71 \pm 0.04$	7.21	55.52	$20.01 \pm 0.02$	$19.35 \pm 0.03$	3.30

The core-shell structure of confined  $CO_2$  is also quantified by taking snapshots of the equilibrated  $CO_2$  molecules adsorbed on the pore surface, see Figure S2.



**Figure S2.** Snapshots showing the anisotropic distribution of  $CO_2$  in MCM-41 and SBA-15 as a function of the pressure. The snapshots are taken during the last 1 ns of the simulation time.

The used model was developed to study the scattering intensity for hexagonally packed cylindrical mesopores with gas adsorbed inside these pores. The scattering intensity (I(q)) of MCM-41 and SBA-15 was expressed as following:

$$\lim_{q_{h,k}L\to\infty} I(q_{h,k}) = C \sum_{h,k} \left\{ \frac{1}{q_{h,k}} m_{h,k} \times \left[ \sum_{0}^{2\pi} d\delta' \int_{0}^{\infty} dq'_{r} q'_{r} \frac{2J_{1}(q_{h,k}R_{m})}{q'_{r}R_{m}} \exp\left[ -\frac{(\sigma q_{h,k})^{2}}{2} \right] - \rho_{ads} 2\pi^{2} R_{v}^{2} R_{m}^{2} \right] \frac{2J_{1}(\sqrt{q_{h,k}^{2} + q'_{r}^{2} - 2q_{h,k}q'_{r}\cos(\delta')R_{v})}{\sqrt{q_{h,k}^{2} + q'_{r}^{2} - 2q_{h,k}q'_{r}\cos(\delta')R_{v}} \right] - \rho_{m} R_{m}^{2} \frac{2J_{1}(q_{h,k}R_{m})}{q_{h,k}R_{m}} \exp\left[ -\frac{(\sigma q_{h,k})^{2}}{2} \right] \frac{2J_{1}(\sqrt{q_{h,k}^{2} + q'_{r}^{2} - 2q_{h,k}q'_{r}\cos(\delta')R_{v})}{\sqrt{q_{h,k}^{2} + q'_{r}^{2} - 2q_{h,k}q'_{r}\cos(\delta')R_{v}}} \right]$$

Where *q* is the wave vector,  $J_1$  is the first-order Bessel function,  $R_m$  is the nominal radius of matrix pore and  $R_v$  is the radius of gas vapor core.  $m_{h,k}$  is the multiplicity, *C* is a constant prefactor related to the length and number density of the cylindrical mesopores and  $\sigma$  is a diffusive parameter characterizing the roughness of the pore wall.  $\rho_v$ ,  $\rho_{ads}$ , and  $\rho_m$  are neutron scattering length densities of the gas vapor core, adsorbed gas and silica matrix, respectively (see Figure S3).



**Figure S3.** Schematic of the cross section of cylindrical pore loaded with gas showing the core radius ( $R_v$ ), matrix radius ( $R_m$ ) and the shell thickness ( $t_{shell}$ ).

The model was first fitted for empty pores (under vacuum where vapor radius and the scattering length density of the adsorbed gas is zero) to govern the parameters *C*,  $\sigma$  and *R*<sub>m</sub> as follows:

$$\lim_{q_{h,k}L\to\infty} I(q_{h,k}) = C \sum_{h,k} \left\{ \frac{1}{q_{h,k}} m_{h,k} \left[ \rho_{Silica} R_m^2 \frac{2J_1(q_{h,k}R_m)}{q_{h,k}R_m} \exp\left[-\frac{(\sigma q_{h,k})^2}{2}\right] \right\} \right\}$$

These parameters (i.e., *C*,  $\sigma$  and *R<sub>m</sub>*) are fixed as constant values for the gas adsorbed fitting cases (i.e., the cases of finite pressure values (> vacuum)). The fitting procedures are explained in detail by Chiang and co-workers.<sup>1,2</sup>

## S3. Energetics of CO<sub>2</sub> adsorption on pore surfaces

The number of hydrogen bond of confined  $CO_2$  with OH groups on the surface as a function of the pressure are listed in **Table S3**. The electrostatic and van der Waals interactions between  $CO_2$  molecules in confinement as a function of the pressure are listed in **Table S4**.

**Table S3.** The number of hydrogen bonds between CO<sub>2</sub> molecules and OH groups on the surface of silica pores as a function of the pressure. Error bars represent the standard deviation from the mean values of three different simulations.

Μ	CM-41	SBA-15		
Pressure (bar)	# Hydrogen bonds	Pressure (bar)	# Hydrogen bonds	
0.98	$3 \pm 1$	0.93	$14 \pm 3$	
14.92	$11 \pm 1$	15.39	$34 \pm 2$	
24.88	$19 \pm 3$	24.95	$49 \pm 4$	
34.72	$34 \pm 2$	34.91	61 ± 3	
44.89	$51 \pm 4$	44.98	$72 \pm 5$	
54.89	$63 \pm 6$	55.52	$85 \pm 3$	

P (bar)	Electrostatic	Van der Waals		
MCM-41				
0.98	$-13.7\pm0.1$	$-17.9\pm0.6$		
14.92	$-42.3\pm0.1$	$-150.8\pm3.9$		
24.88	$-75.4\pm0.3$	$-432.8\pm9.3$		
34.72	$-150.4\pm0.1$	$-1,215.7 \pm 3.1$		
44.89	$-232.6\pm0.1$	$-2,132.3 \pm 1.0$		
54.89	$-313.1 \pm 0.1$	$-3,148.4 \pm 0.2$		
SBA-15				
0.93	$-181.9\pm1.4$	$-1,282.8 \pm 46.0$		
15.39	$-246.4 \pm 2.4$	$-1,896.4 \pm 72.0$		
24.95	$-454.1 \pm 1.5$	$-4,088.0 \pm 42.1$		
34.91	$-583.1\pm0.3$	$-5,468.3 \pm 7.5$		
44.98	$-1,178.5 \pm 0.2$	$-12,345.1 \pm 1.0$		
55.52	$-2,783.4 \pm 6.3$	$-22,791.4 \pm 4.6$		

**Table S4.** The electrostatic and van der Waals interactions (kJ/mol) of CO2-CO2 as a function of<br/>the pressure.

#### References

- W. S. Chiang, E. Fratini, P. Baglioni, D. Georgi, J.H. Chen and Y. Liu, Methane adsorption in model mesoporous material, SBA-15, studied by small-angle neutron scattering, *J. Phys. Chem. C*, 2016, **120**, 4354-4363.
- 2. W. S. Chiang, E. Fratini, P. Baglioni, J.H. Chen and Y. Liu, Pore size effect on methane adsorption in mesoporous silica materials studied by small-angle neutron scattering, *Langmuir*, 2016, **32**, 8849-8857.