Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Molecular insight into the high selectivity of double-walled carbon nanotubes

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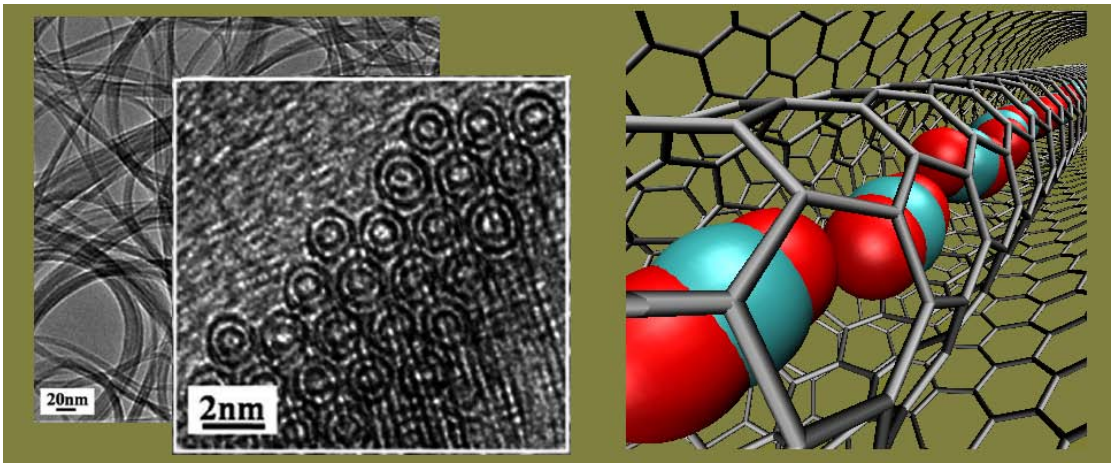

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1. Force fields

	σ_{ff} (Å)	ε_{ff}/k_B (K)	l_{CO} (Å)	l_q (e)
Carbon dioxide	C: 2.824 O: 3.026 C-O: 2.925	C: 28.68 O: 82.0 C-O: 48.495	1.162	C: 0.664 O: -0.332

Table 1. Lennard-Jones parameters and partial charges for the 3-site carbon dioxide model: C-O denotes LJ parameters obtained from Lorentz-Berthelot mixing rule, l_{CO} is the C-O bond length.

	σ_{ff} (Å)	ε_{ff}/k_B (K)	l_{CH} (Å)	l_q (e)
Methane	C: 3.4 H: 2.65 C-H: 3.025	C: 55.055 H: 7.901 C-H: 30.6	1.09	H: 0.165 C: -0.66

Table 2. Lennard-Jones parameters and partial charges for the 5-site methane model: C-H denotes LJ parameters fitted to experimental data, l_{CH} is the C-H bond length.

	σ_{ff} (Å)	ε_{ff}/k_B (K)	l_{OO} (Å)	l_q (e)
Oxygen	O: 3.1062	O: 43.183	0.9699	O: -0.40405 COM: 0.8081

Table 3. Lennard-Jones parameters and partial charges for the 2-site oxygen model: COM denotes centre of mass, l_{OO} is the O-O bond length.

	σ_{ff} (Å)	ε_{ff}/k_B (K)	l_{NN} (Å)	l_q (e)
Nitrogen	N: 3.31	N: 36.0	1.1	N: -0.482 COM: 0.964

Table 4. Lennard-Jones parameters and partial charges for the 2-site nitrogen model: COM denotes centre of mass, l_{NN} is the N-N bond length.

	σ_{ff} (Å)	ε_{ff}/k_B (K)	l_{HH} (Å)	l_{LL} (Å)	l_q (e)
Hydrogen	L: 2.37031 COM: 3.15528 L-COM: 2.762795	L: 2.16726 COM: 12.76532 L-COM: 5.259826	0.742	0.726	H: 0.3732 COM: -0.7464

Table 5. Lennard-Jones parameters and partial charges for the 5-site hydrogen model: COM denotes centre of mass, L is the additional LJ site, l_{HH} is the H-H bond length, l_{LL} is the L-L bond length, L-COM denotes LJ parameters obtained from Lorentz-Berthelot mixing rule.

	σ_{ff} (Å)	ε_{ff}/k_B (K)	l_{CO} (Å)	l_q (e)
Carbon monoxide	C: 3.49 O: 3.13 C-O: 3.31	C: 22.8 O: 63.5 C-O: 38.05	1.128	C: 0.0203 O: -0.0203

Table 6. Lennard-Jones parameters and partial charges for the 2-site carbon monoxide model: C-O denotes LJ parameters obtained from Lorentz-Berthelot mixing rule, l_{CO} is the C-O bond length.

2. Force fields validation using thermodynamics data

We estimated the average density from the following expression,

$$\rho\left(\mathrm{mmol\,cm^{-3}}\right)=10000\langle\rho\rangle/6.0223 \tag{1S}$$

where $\langle...\rangle$ denotes an ensemble average, $\langle\rho\rangle=N/\langle V(\text{Å})\rangle$ is the average number density, and N denotes a number of molecules. Additionally, for selected adsorbates and state points, we computed isothermal compressibility and coefficient of thermal expansion from the fluctuation formulas,

$$\kappa=-1/V\left(\partial V/\partial p\right)_{N,T}=\left(\langle V^2\rangle-\langle V\rangle^2\right)/k_bT\langle V\rangle \tag{2S}$$

$$\alpha=1/V\left(\partial V/\partial T\right)_{N,p}=\left(\langle VH\rangle-\langle V\rangle\langle H\rangle\right)/k_bT^2\langle V\rangle \tag{3S}$$

$$H=E(fluid)+pV=\sum_{a<b}E_{ab}+pV \tag{4S}$$

where E_{ab} is the total potential energy between particle a and b, T denotes temperature, p is the pressure, H is the enthalpy, R is the universal gas constant, and k_b denotes Boltzmann constant.

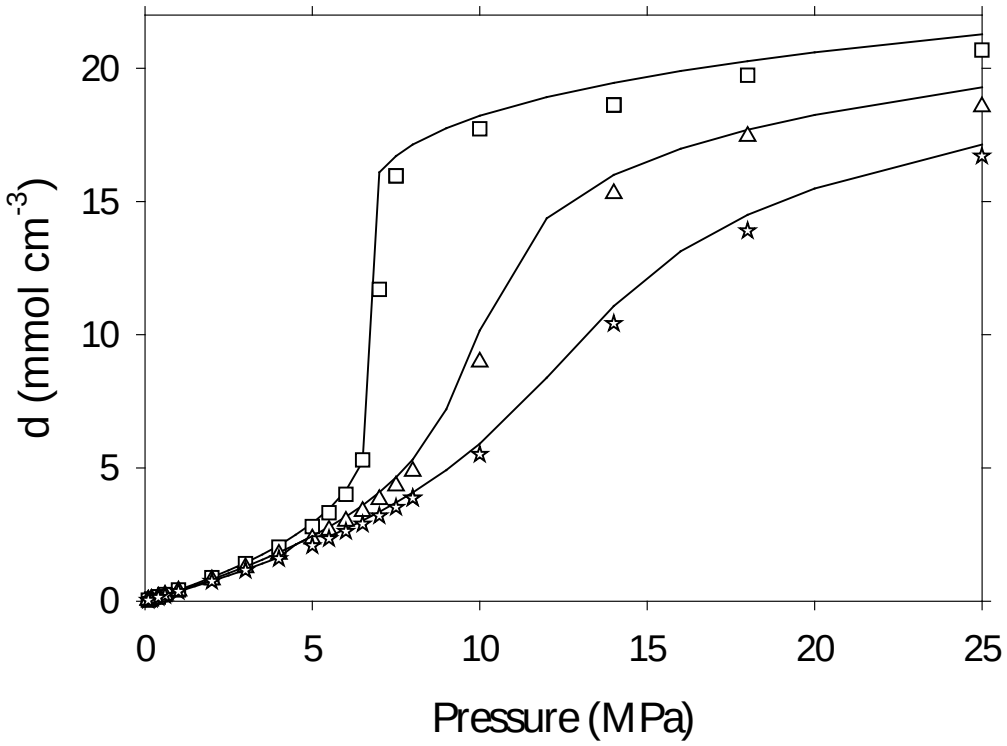

Figure 1S. Comparison of the experimental equation of states for carbon dioxide (solid lines) with the results calculated from isothermal-isobaric Monte Carlo simulations at 298 (open squares), 320 (open triangles), and 340 K (open stars).

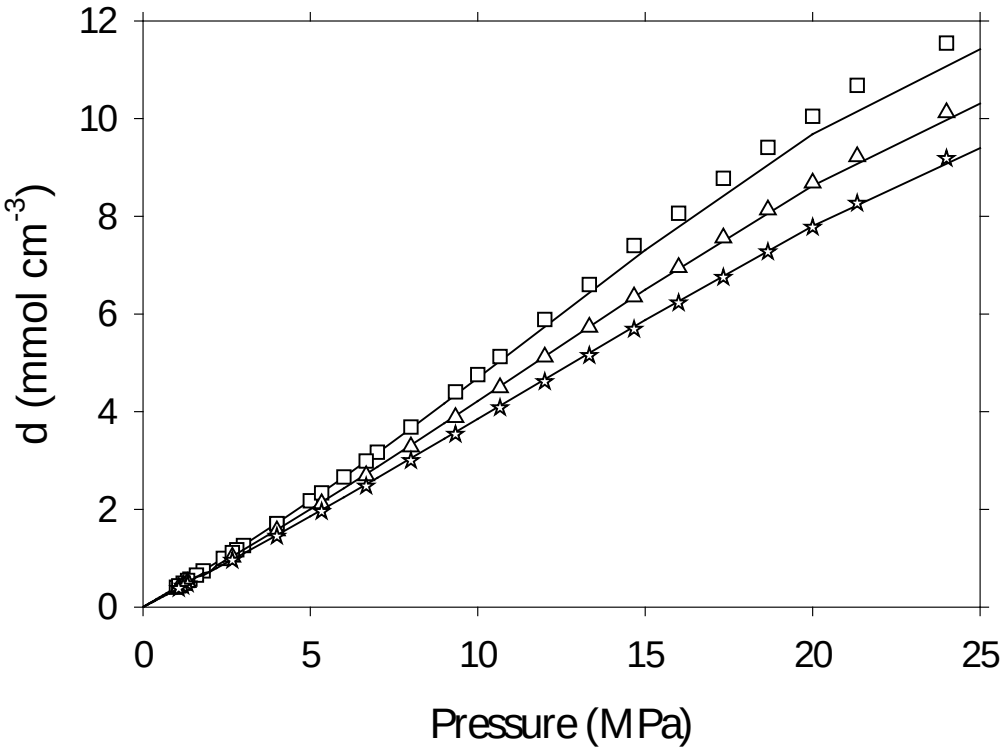

Figure 2S. Comparison of the experimental equation of states for methane (solid lines) with the results calculated from isothermal-isobaric Monte Carlo simulations at 298 (open squares), 320 (open triangles), and 340 K (open stars).

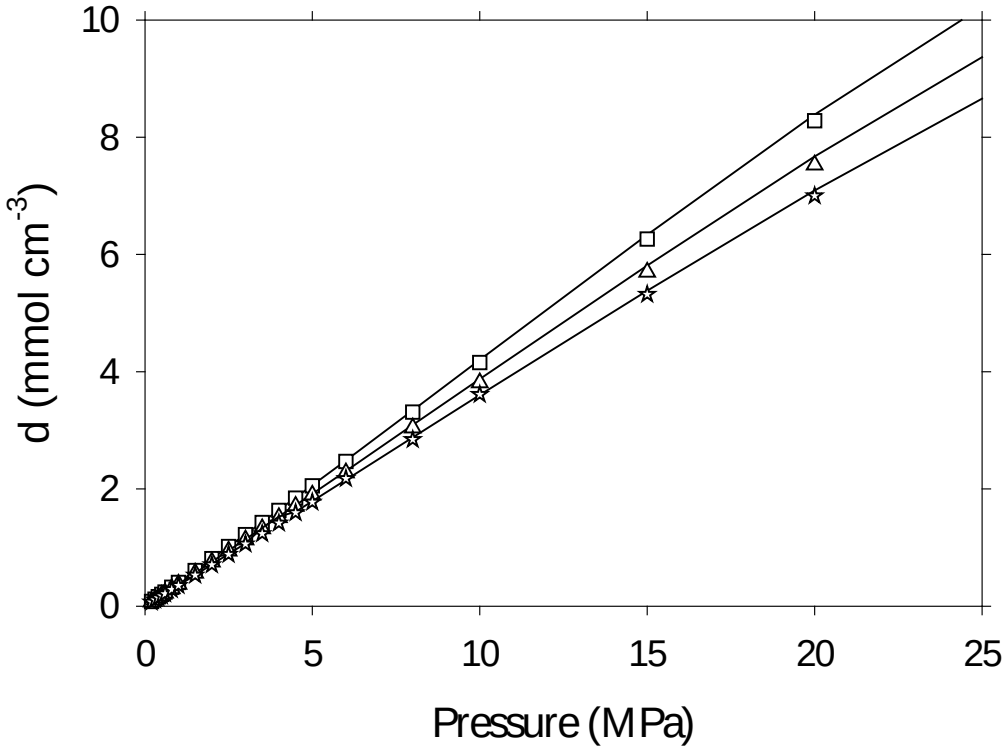

Figure 3S. Comparison of the experimental equation of states for oxygen (solid lines) with the results calculated from isothermal-isobaric Monte Carlo simulations at 298 (open squares), 320 (open triangles), and 340 K (open stars).

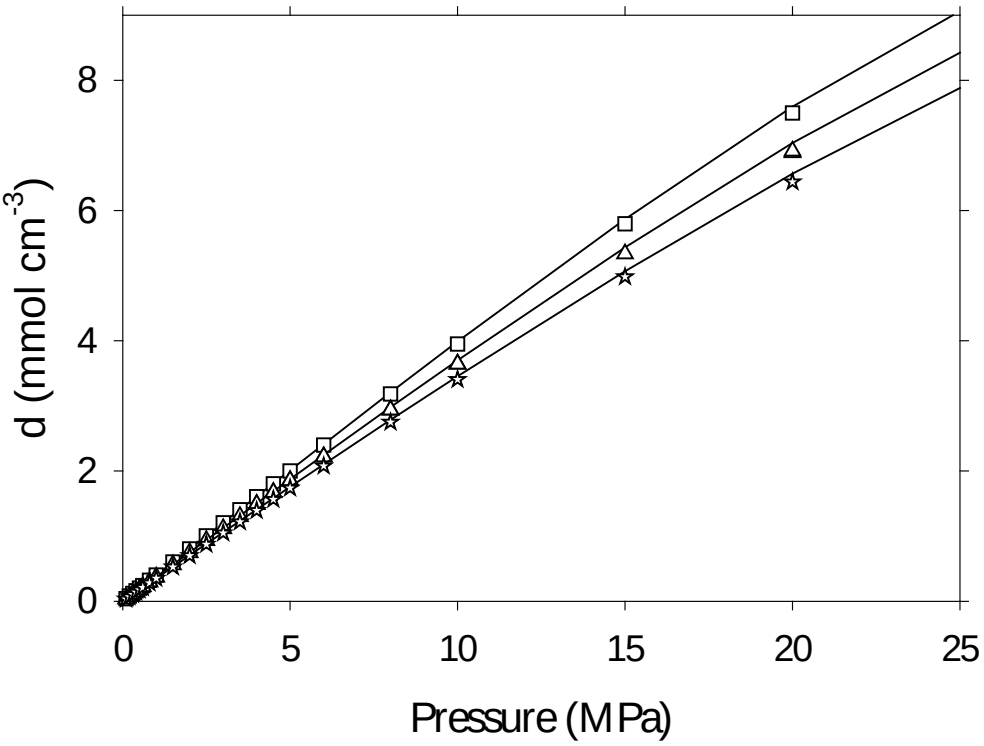

Figure 4S. Comparison of the experimental equation of states for nitrogen (solid lines) with the results calculated from isothermal-isobaric Monte Carlo simulations at 298 (open squares), 320 (open triangles), and 340 K (open stars).

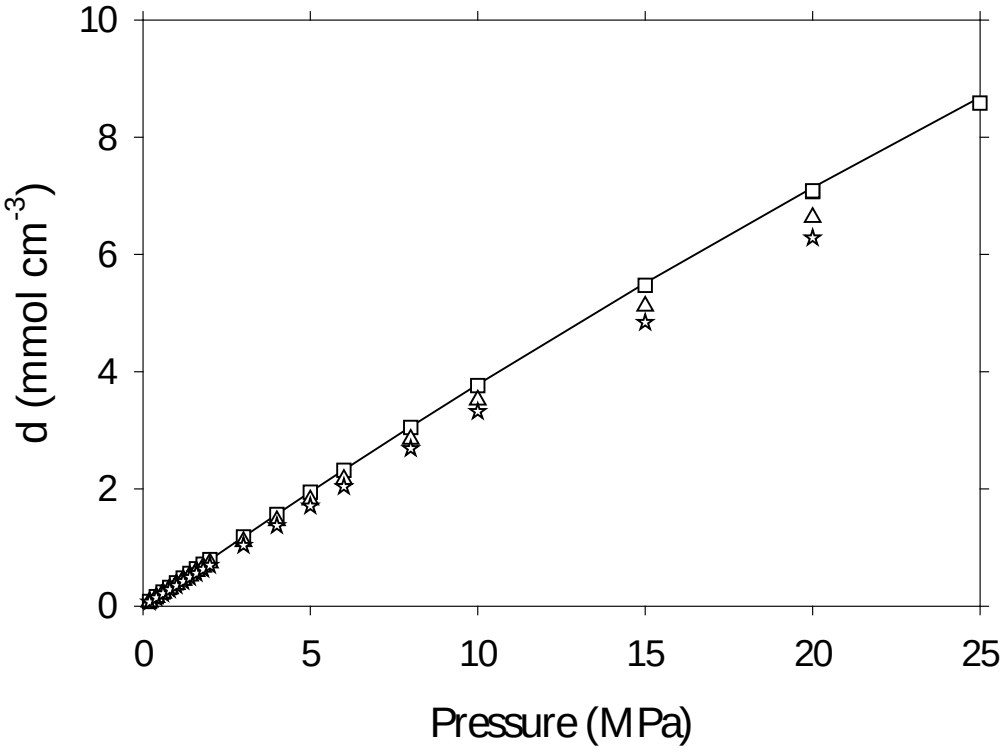

Figure 5S. Comparison of the experimental equation of state for hydrogen at 298 K (solid line) with the results calculated from isothermal-isobaric Monte Carlo simulations at 298 (open squares), 320 (open triangles), and 340 K (open stars).

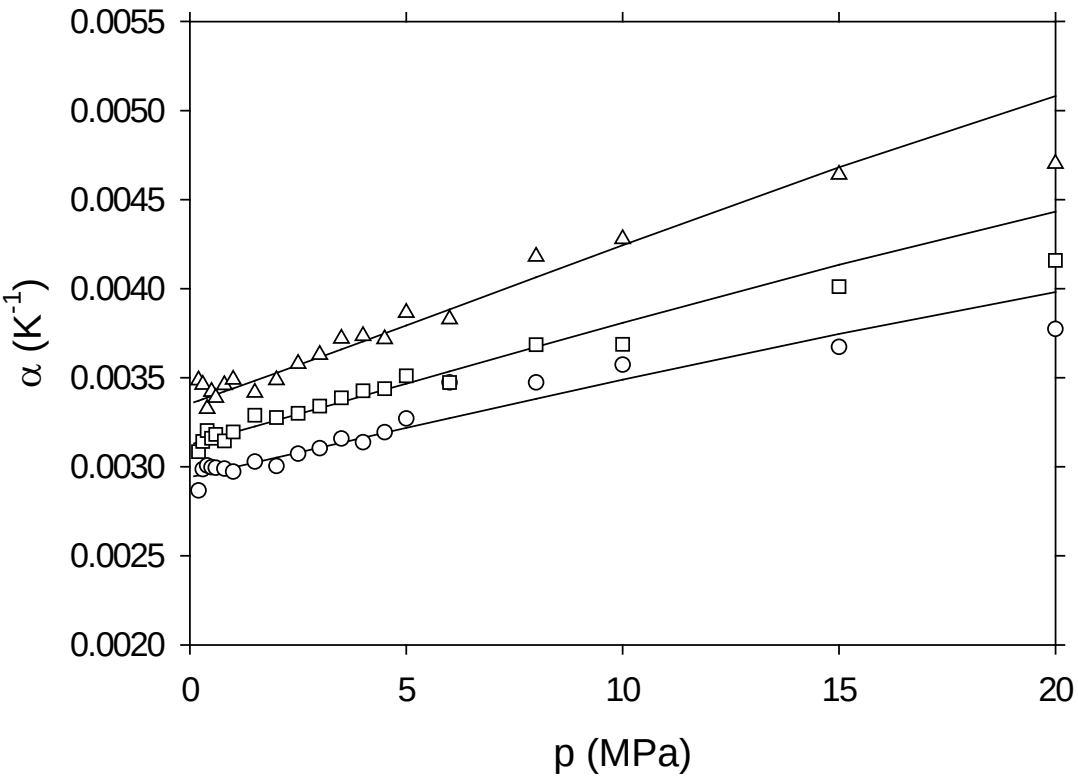

Figure 6S. The comparison of the experimental thermal expansivity of oxygen (solid lines) with the results calculated from isothermal-isobaric Monte Carlo simulations at 298 (triangles), 320 (squares), and 340 K (circles).

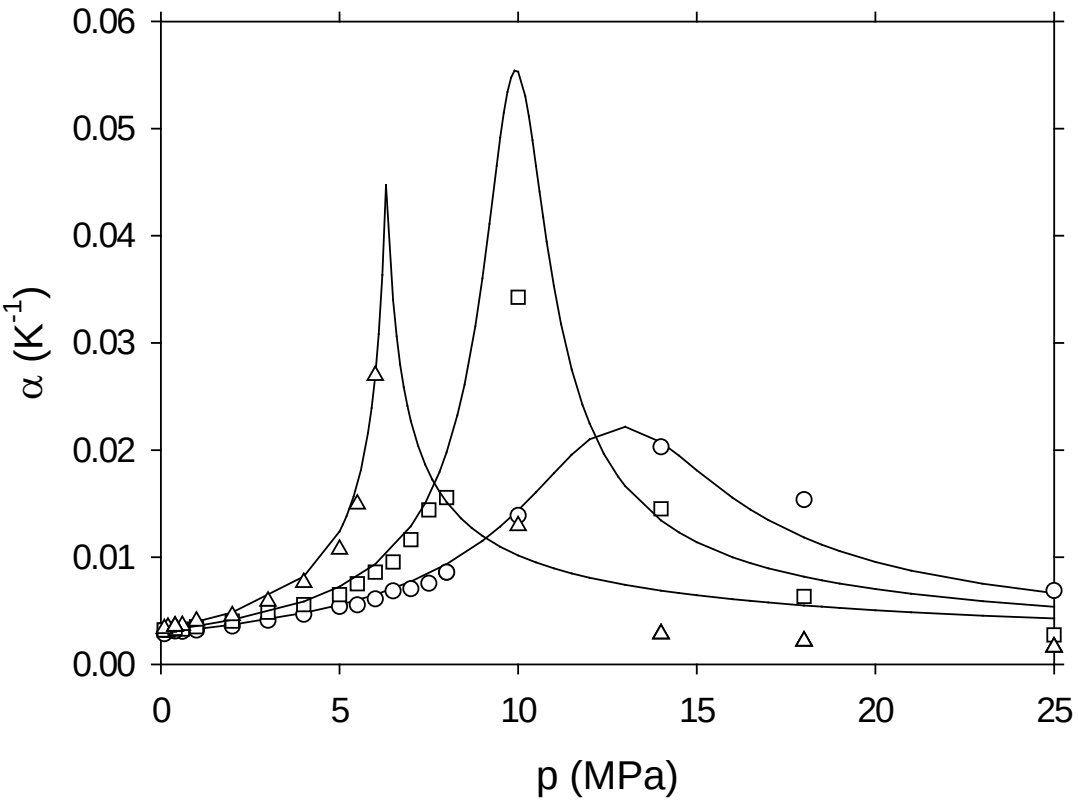

Figure 7S. The comparison of the experimental thermal expansivity of carbon dioxide (solid lines) with the results calculated from isothermal-isobaric Monte Carlo simulations at 298 (triangles), 320 (squares), and 340 K (circles).

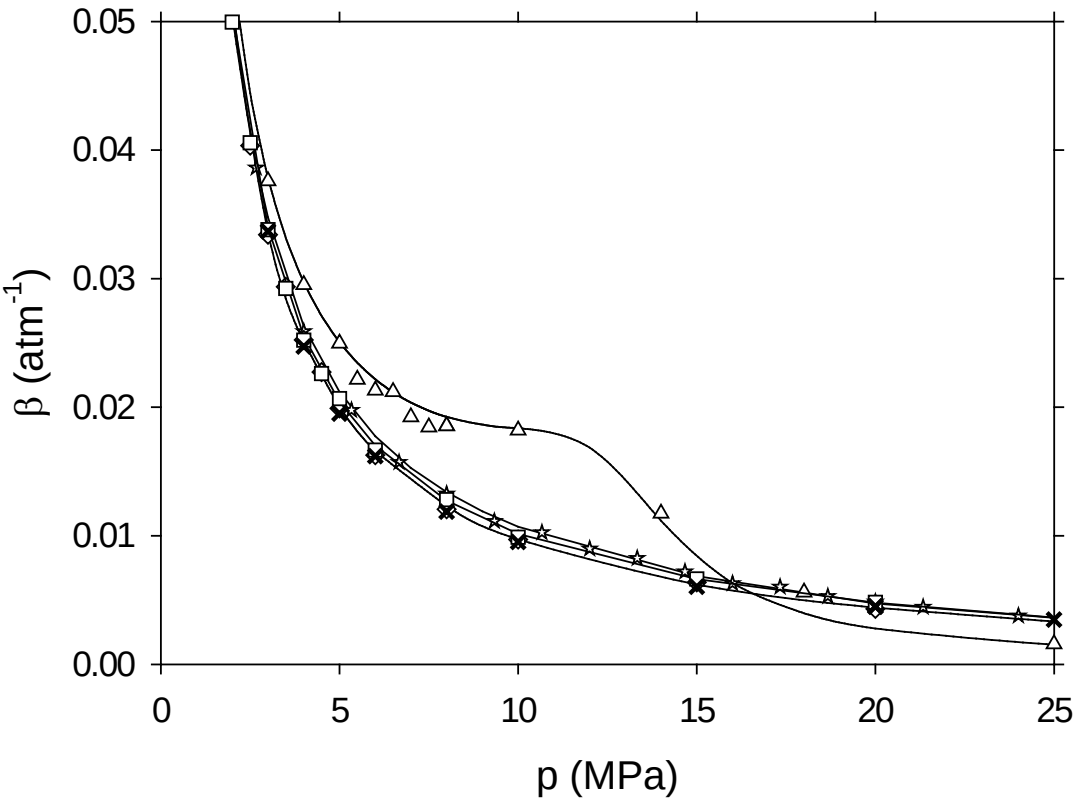

Figure 8S. Comparison of the experimental isothermal compressibility for carbon dioxide, methane, oxygen, and nitrogen (solid lines) at 340 K with the results calculated from isothermal-isobaric Monte Carlo simulations: triangles-carbon dioxide, stars-methane, squares-oxygen, diamonds-nitrogen, and crosses-hydrogen.

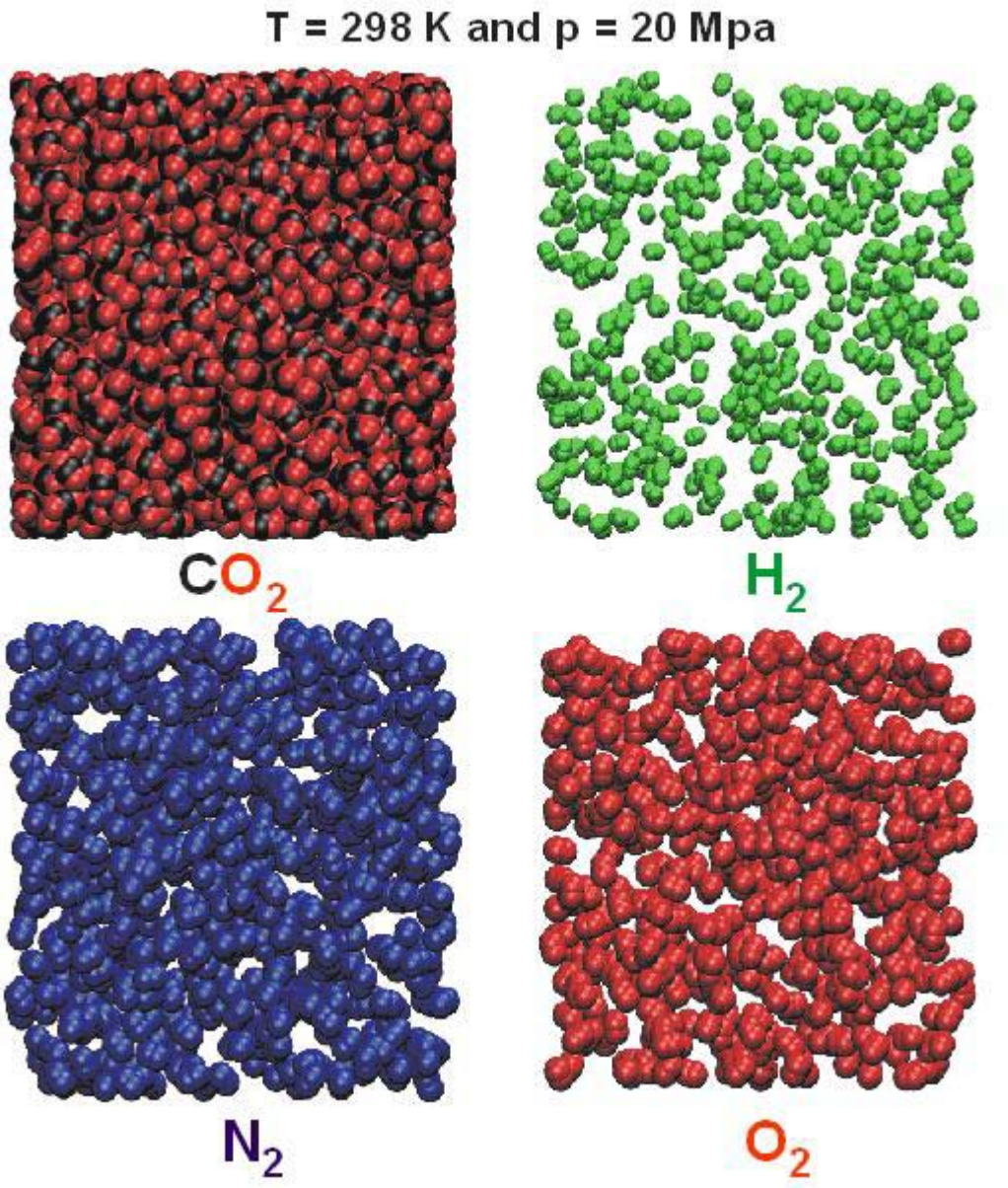

Figure 9S. Atomistic structure of CO_2, H_2, N_2, and O_2 at 298 K and 20 MPa computed from isothermal-isobaric Monte Carlo simulations.