Electronic Supplementary Information

What are the key factors governing the nucleation of CO_2 hydrate?

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Simulation Methods

In a previous study, we conducted microsecond molecular dynamics (MD) simulations on the nucleation and growth of CH_4/CO_2 mixed hydrates from two-phase systems of water and CH_4/CO_2 gas mixture.[1] At that time, we also performed simulations to explore the nucleation of CO_2 hydrate from water/CO_2 two-phase system at 250 K and 50 MPa using the TIP4P-Ice water model and the EPM2 CO_2 model; however, the nucleation was not observed even though the simulation duration was up to 7 μs, as shown in Fig. S1. In the current study, we therefore attempt to unravel the key factors governing the nucleation of CO_2 hydrate.

In a cubic box with an initial length of 5 nm, 512 CO_2 molecules and 2944 water molecules were randomly mixed to form a homogenous system. The composition of the system was the same as a sI crystalline hydrate. The system was initially equilibrated under isothermal-isobaric (NPT) ensemble at 300 K and 10 MPa for 20 ns to spontaneously form a spherical CO_2 phase in water. Such a two-phase system (Fig. S2A), as the starting configuration, was cooled and pressurized to 250 K and 50 MPa, and simulated for up to several μs to examine CO_2 hydrate nucleation. The TIP4P-Ice model[2] was used for water and the cross-interaction parameters between water and CO_2 were calculated by the Lorentz-Berthelot combining rules. As mentioned above, CO_2 hydrate nucleation did not occur using the EPM2 CO_2 model[3] (Fig. S1A, S1C, S1E and S1F). Subsequently, the TraPPE CO_2 model[4] was tested but nucleation did not occur either (Fig. S1B, S1D, S1E and S1G). Recently, Costandy *et al.*[5] examined a series of water models and CO_2 models to simulate the phase equilibria of CO_2 hydrate; they found that the three-phase coexistence temperature of CO_2 hydrate and the solubility of CO_2 in water could be accurately predicted by using the TraPPE CO_2 model and the TIP4P-Ice model *with the well depth between the oxygen in CO_2 and the oxygen in water $\varepsilon_{O(CO2)\text{-}O(H2O)}$ scaled by a factor of 1.08*. Thus, we used these optimized parameters to explore CO_2 hydrate nucleation and found that CO_2 hydrate nucleation occurred, with a pre-nucleation CO_2 mole fraction in water x_{CO_2} (about 0.080) higher than the cases using the EPM2 (about 0.068) and TraPPE (about 0.064) CO_2 models. These results unravel that a high aqueous guest concentration is required to trigger CO_2 hydrate nucleation. Repeat runs were performed (2 runs using the EPM2 or TraPPE CO_2 models and 5 runs using the optimized parameters). To further explore whether CO_2 hydrate nucleation can occur at a lower x_{CO_2} using the optimized parameters, we manually set up a water/slab CO_2 two-phase system as the starting configuration (Fig. S2B). This system also contained 512 CO_2 molecules and 2944 water molecules and its box size was $3.46\times3.46\times11.00$ nm^3. It showed a lower x_{CO_2} (about 0.060) than the water/spherical CO_2 two-phase system (about 0.080), due to the lower Yong-Laplace pressure at the planar water/CO_2 interface. Additionally, the simulation results on CH_4 hydrate nucleation from our previous study[1] were used to compare the nucleation of CO_2 and CH_4 hydrates at the same condition (512 CH_4 and 2944 water molecules at 250 K and 50 MPa).

To confirm that a high aqueous guest concentration is required for CO_2 hydrate nucleation and quantitatively determine the critical CO_2 concentration for nucleation (especially in the simulations using the EPM2 or TraPPE CO_2 models, where nucleation did not occur), we set up a series of homogenous CO_2 solution systems as starting

configurations to examine CO_2 hydrate nucleation at 250 K and 50 MPa. 2944 water molecules and different number of CO_2 molecules (512, 479, 440, 401, 364, 327, 291, 256, 222, 188 and 155 CO_2) were randomly placed in a cubic box to form homogenous CO_2 solution systems with different x_{CO_2}. The EPM2, TraPPE CO_2 models and the optimized CO_2–water parameters were used and the simulation duration was at least 500 ns. Note that during the simulations, x_{CO_2} was lower than that in the starting configurations, as some CO_2 molecules aggregated to form small clusters. Particularly, a large CO_2 phase formed in the system with the highest CO_2 supersaturation (512 CO_2) using the EPM2 and TraPPE CO_2 models, see Fig. S1H and Fig. S9F. Table S1 summarizes the simulation systems in this study.

Table S1. Summary of the simulation systems in this study.[a]

System	Runs	CO_2 model	Water model	Combining rule	x_{CO_2}	Nucleation state
Water/Spherical CO_2	2	EMP2	TIP4P-Ice	Lorentz-Berthelot	0.068	not nucleated
Water/Spherical CO_2	2[b]	TraPPE	TIP4P-Ice	Lorentz-Berthelot	0.064	not nucleated
Water/Spherical CO_2	5	TraPPE	TIP4P-Ice	$1.08*\varepsilon_{O(CO2)-O(H2O)}$	0.080	nucleated
Water/Slab CO_2	2	TraPPE	TIP4P-Ice	$1.08*\varepsilon_{O(CO2)-O(H2O)}$	0.060	not nucleated
CO_2 solutions	1	EMP2	TIP4P-Ice	Lorentz-Berthelot	No. of CO_2 188-512	nucleated at x_{CO_2} >= 0.088
CO_2 solutions	1	TraPPE	TIP4P-Ice	Lorentz-Berthelot	No. of CO_2 188-512[b]	attempts at x_{CO_2} = 0.086, 0.090 nucleated at x_{CO_2} >= 0.092
CO_2 solutions	1	TraPPE	TIP4P-Ice	$1.08*\varepsilon_{O(CO2)-O(H2O)}$	No. of CO_2 155-512	nucleated at x_{CO_2} >= 0.088

[a]All the systems contained 2944 water molecules. x_{CO_2} is pre-nucleation mole fraction of CO_2 in water; the number of CO_2 molecules is indicated for the CO_2 solution systems. [b]In the CO_2 solution system containing 512 CO_2 (using the TraPPE model), CO_2 molecules quickly evolved in to a spherical CO_2 phase (Fig. S1H), thus this system was considered as a water/spherical CO_2 system.

All the simulations were performed at 250 K and 50 MPa using GROMACS v.5.0.6.[6] Constant temperature and pressure were regulated by the Nosé-Hoover thermostat[7] with a time constant of 2.0 ps and the Parrinello-Rahman barostat[8] with a time constant of 4.0 ps, respectively. The periodic boundary conditions were imposed in three directions. A cutoff of 1.0 nm was used to estimate the short-range non-bonded interactions with the long-range corrections applied to energy and pressure. The electrostatic interactions were calculated with particle mesh Ewald method.[9] The SETTLE algorithm[10] was used to constrain the rigid geometry of water molecules. Trajectories were integrated using the leapfrog scheme with a time step of 2 fs and coordinates were stored every 10 ps.

As different CO_2 models and combining rules were tested to simulate CO_2 hydrate nucleation, the names of the CO_2 models are indicated in the figure captions. "**TIP4P-Ice_EPM2**" means the TIP4P-Ice water model, the EPM2 CO_2 model and the Lorentz-Berthelot combining rules for CO_2-water interaction were used. "**TIP4P-Ice_TraPPE**" means the TIP4P-Ice water model, the TraPPE CO_2 model and the Lorentz-Berthelot combining rules for CO_2-water interaction were used. "**TIP4P-Ice_1.08*TraPPE**" means the TIP4P-Ice water model, the TraPPE CO_2 model and *the well depth between the oxygen in CO_2 and the oxygen in water $\varepsilon_{O(CO2)-O(H2O)}$ scaled by a factor of 1.08* for CO_2-water interaction were used.

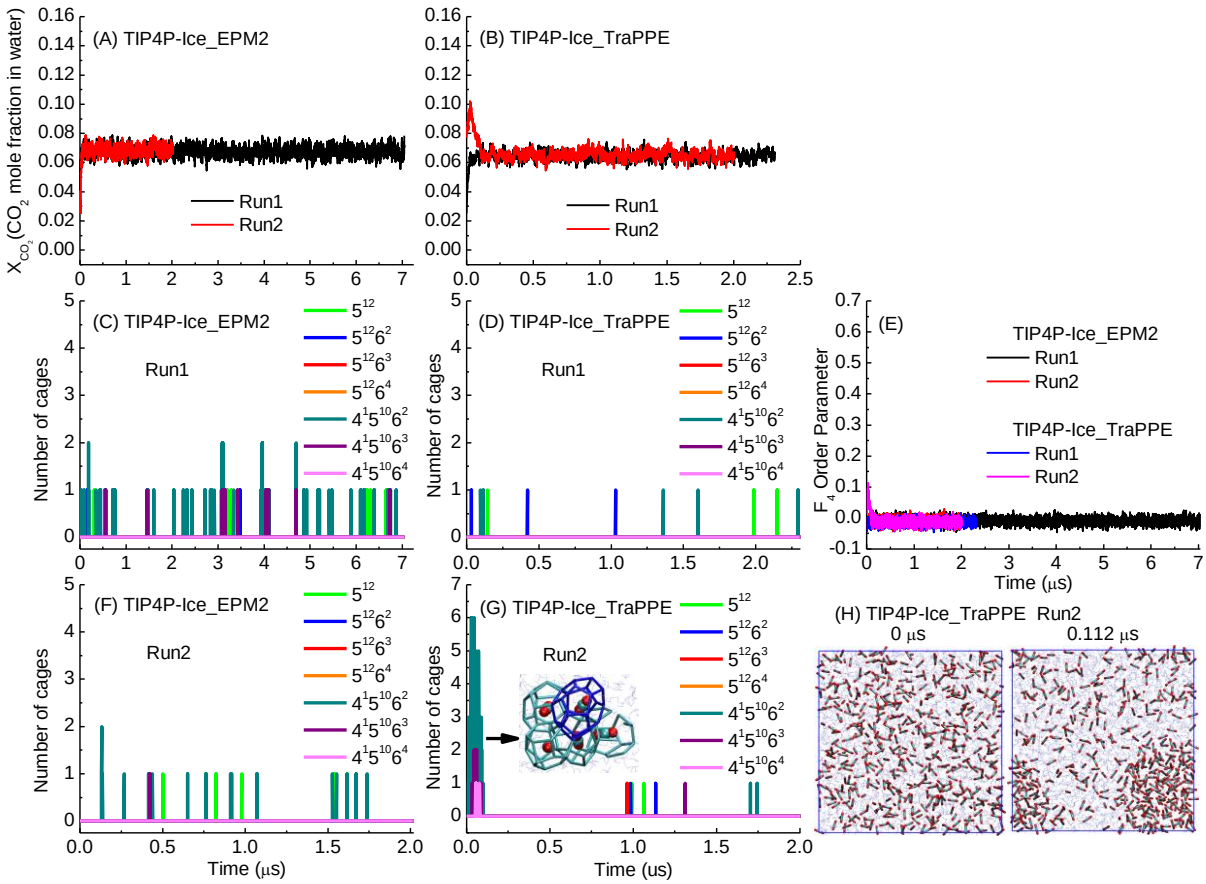

Fig. S1 Evolution of CO_2 mole fraction in water x_{CO_2}, F_4 order parameter (E), and cage number during the simulations using the Lorentz-Berthelot combining rules, TIP4P-Ice water model, EPM2 CO_2 model (A,C,F) or TraPPE CO_2 model (B,D,G) at 250 K and 50 MPa. All the starting configurations of these simulations contained water/CO_2 two phases, except in Run2 using TraPPE model, a homogenous CO_2 solution was used as the starting configuration. Note that (H) *in Run2 using TraPPE model, with CO_2 molecules aggregated to form CO_2 phase, the initial cage cluster dissociated* (G) *and* x_{CO_2} *decreased* (B) *to the equilibrated value as in Run1, i.e. Run2 is essentially the same as Run1 in later simulation duration*.

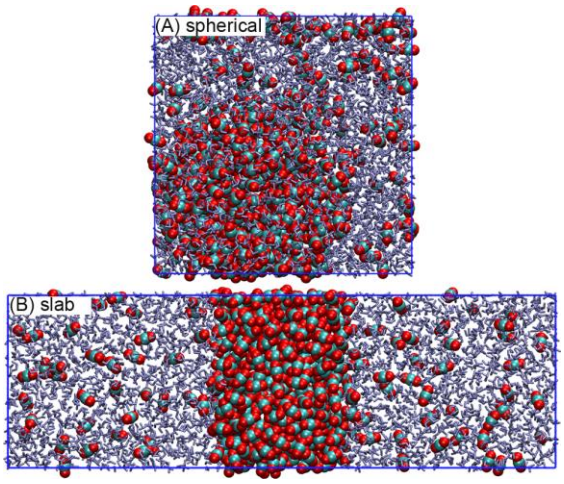

Fig. S2 Starting configurations containing a (A) spherical and (B) slab CO_2 liquid phase. Water molecules are shown as light blue sticks and CO_2 molecules are displayed as red and cyan balls.

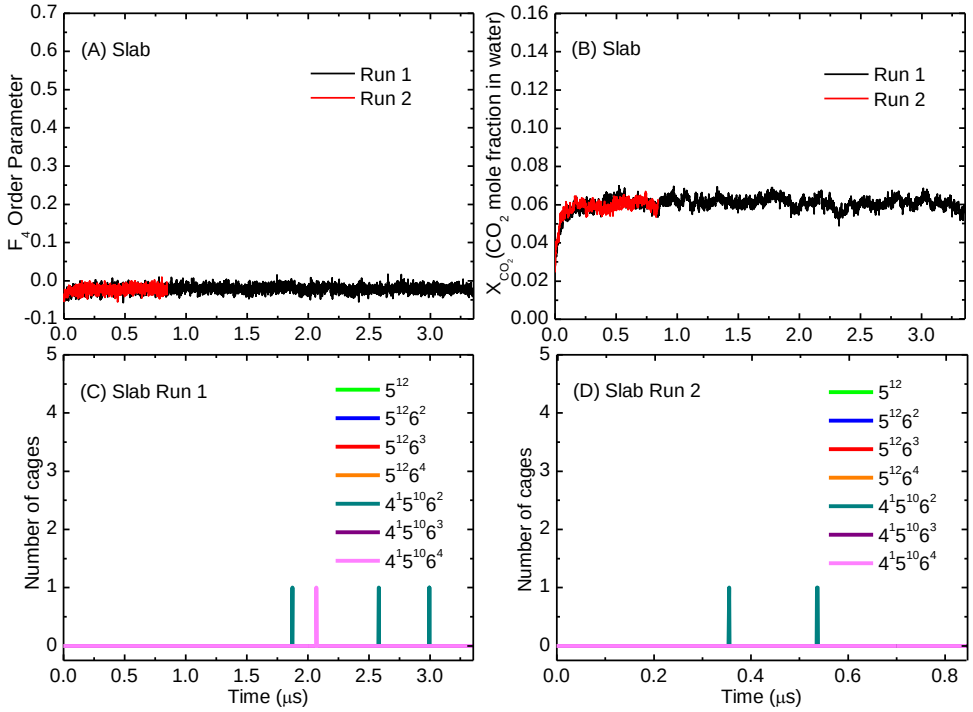

Fig. S3 (**use TIP4P-Ice_1.08*TraPPE**) Entire evolution of (A) F_4 order parameter, (B) CO_2 mole fraction in water x_{CO_2} and (C and D) number of cages for the system with slab CO_2 liquid phase.

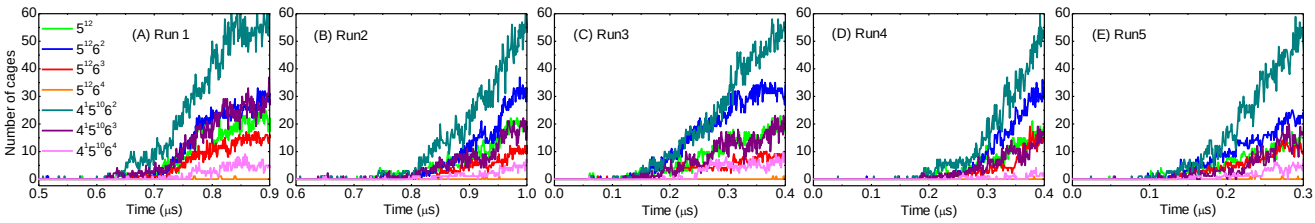

Fig. S4 (**use TIP4P-Ice_1.08*TraPPE**) Evolution of cage numbers during the nucleation and initial growth in the five repeated runs for the system with spherical CO_2 liquid phase.

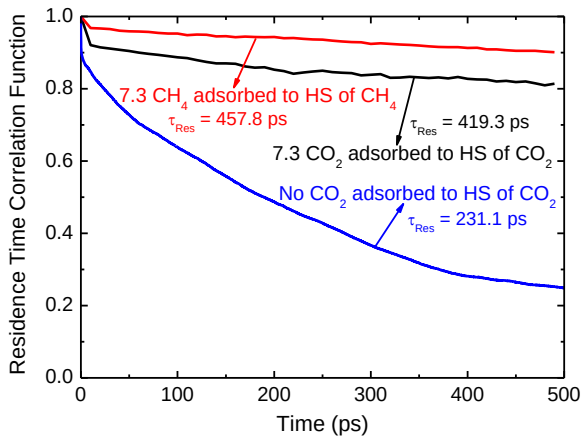

Fig. S5 (**use TIP4P-Ice_1.08*TraPPE**) Residence time correlation functions of water molecules in the hydration shells (HS) of CO_2 and CH_4 with different number of gas molecules adsorbed. The corresponding residence times τ_{Res} are indicated in the figure.

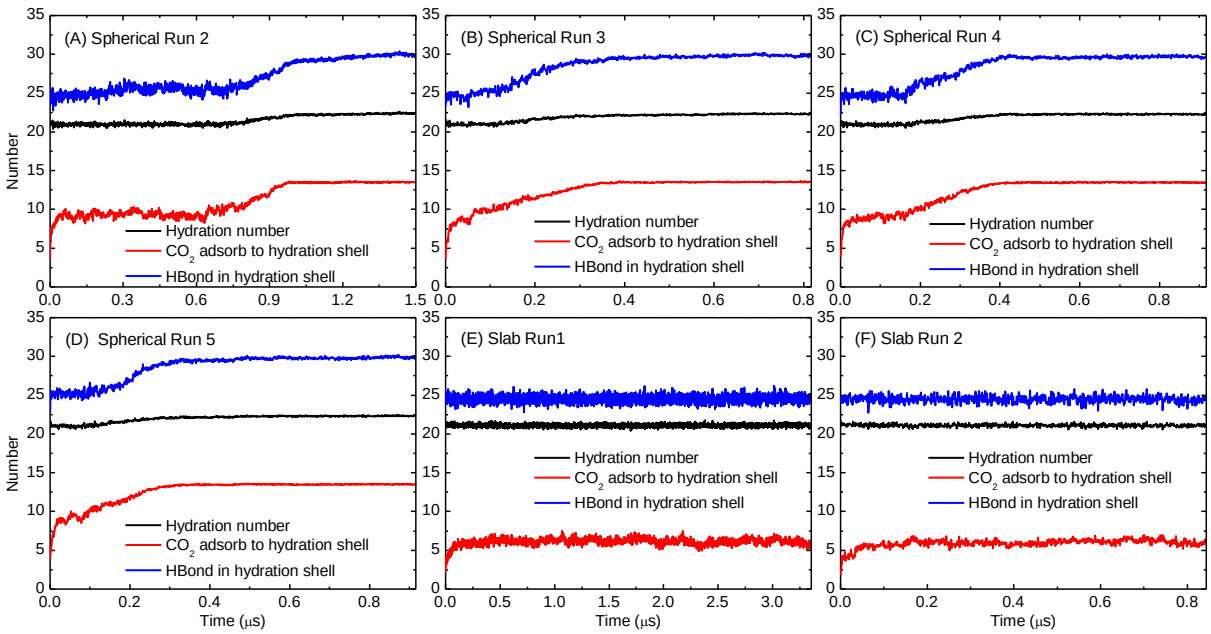

Fig. S6 (**use TIP4P-Ice_1.08*TraPPE**) Evolution of number of hydrogen bonds in CO_2 hydration shells, hydration number and number of CO_2 adsorbed to CO_2 hydration shells during the five repeated runs for the systems containing a spherical (A-D) and slab (E and F) CO_2 liquid phase. These numbers are averaged over all the dissolved CO_2 molecules.

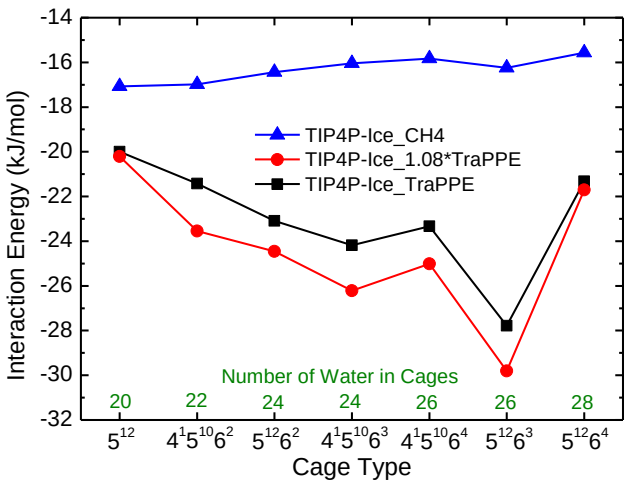

Fig. S7 Interaction energy between a CH_4 or CO_2 molecule and water molecules in the seven types of cages.

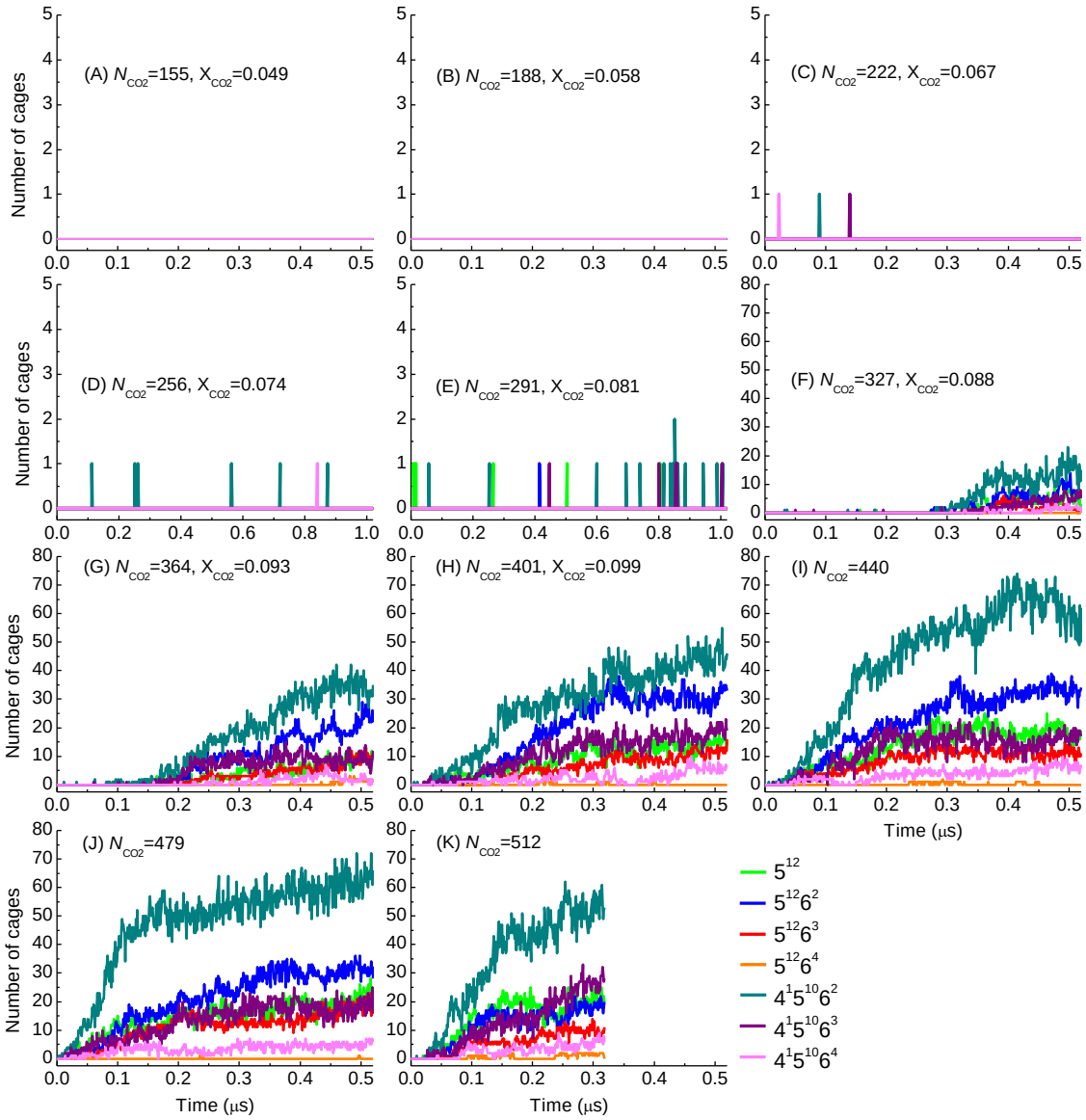

Fig. S8 (**use TIP4P-Ice_1.08*TraPPE**) Evolution of cage numbers during the simulations for CO_2 solution systems with different number of CO_2 (N_{CO_2}) and pre-nucleation x_{CO_2}.

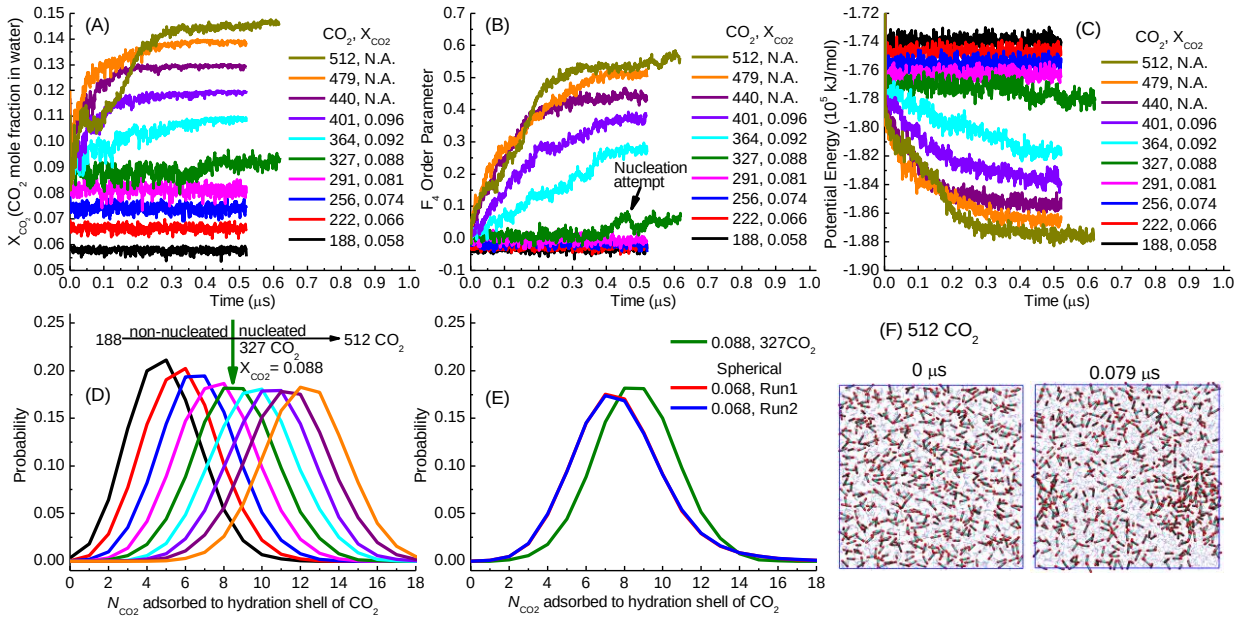

Fig. S9 (**use TIP4P-Ice_EPM2**) High aqueous guest concentration required for the nucleation of CO_2 hydrate. Evolution of (A) CO_2 mole fraction in water x_{CO_2} (B) F_4 order parameter, (C) potential energy and (D) distribution of number of CO_2 adsorbed to CO_2 hydration shells (N_{CO_2}) for CO_2 solution systems. The number of CO_2 in the systems and pre-nucleation x_{CO_2} are indicated in the legends. *Note that only above or equivalent to the critical x_{CO_2} (about 0.088), hydrate nucleation occurs*. (E) Comparing the distributions of N_{CO_2} in the non-nucleated system containing water/liquid CO_2 phase with x_{CO_2} = 0.068 (Fig. S1A) with that in CO_2 solution system with critical x_{CO_2} (0.088). (F) With the highest supersaturation (512 CO_2), some CO_2 molecules aggregate to form CO_2 phase at 0.079-0.1 μs. *Hydrate nucleation attempt was observed in CO_2 solution system with critical x_{CO_2} (0.088).*

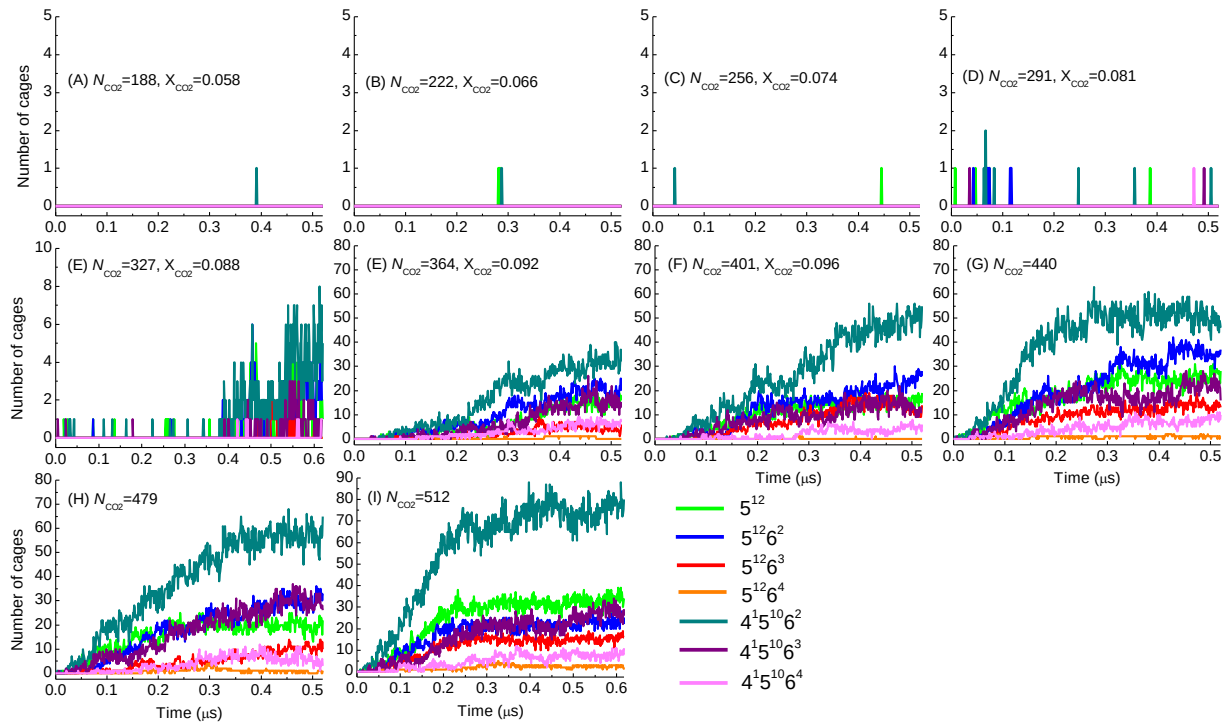

Fig. S10 (**use TIP4P-Ice_EPM2**) Evolution of cage numbers during the simulations for CO_2 solution systems with different number of CO_2 (N_{CO_2}) and pre-nucleation x_{CO_2}.

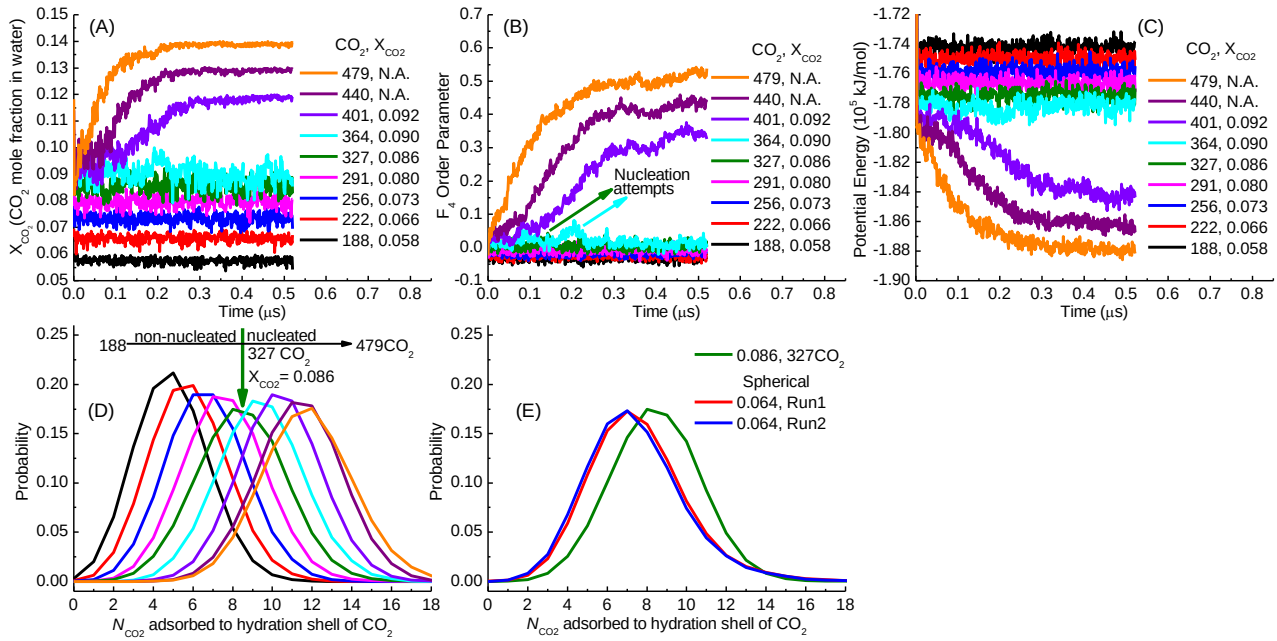

Fig. S11 (**use TIP4P-Ice_TraPPE**) High aqueous guest concentration required for the nucleation of CO_2 hydrate. Evolution of (A) CO_2 mole fraction in water x_{CO_2} (B) F_4 order parameter, (C) potential energy and (D) distribution of number of CO_2 adsorbed to CO_2 hydration shells (N_{CO_2}) for CO_2 solution systems. The number of CO_2 in the systems and pre-nucleation x_{CO_2} are indicated in the legends. *Note that only above or equivalent to the critical x_{CO_2} (about 0.092), hydrate nucleation occurs*. (E) Comparing the distributions of N_{CO_2} in the non-nucleated system containing water/liquid CO_2 phase with x_{CO_2} = 0.064 (Fig. S1B) with that in CO_2 solution system with x_{CO_2} = 0.086. *Note that in (B) hydrate nucleation attempts were observed in CO_2 solution systems with pre-nucleation x_{CO_2} = 0.086 and 0.090.*

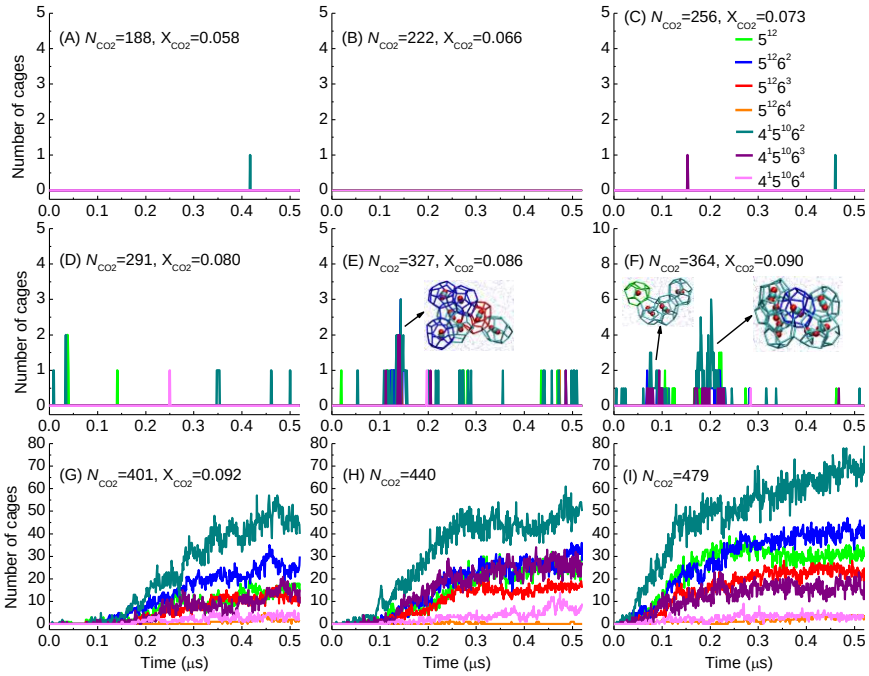

Fig. S12 (**use TIP4P-Ice_TraPPE**) Evolution of cage numbers during the simulations for CO_2 solution systems with different number of CO_2 (N_{CO_2}) and pre-nucleation x_{CO_2}. The insets in (E) and (F) show the cage clusters formed during hydrate nucleation attempts.

Video S1. Nucleation process of CO_2 hydrate. Water molecules and CO_2 (only carbon atom) are represented as light blue thin lines and red balls, respectively. Hydrate cages are shown as sticks with different colors (green for 5^{12}, blue for $5^{12}6^2$, red for $5^{12}6^3$, orange for $5^{12}6^4$, cyan for $4^15^{10}6^2$, purple for $4^15^{10}6^3$ and pink for $4^15^{10}6^4$).

Video S2. Nucleation process of CH_4 hydrate. Water molecules and CH_4 are represented as light blue thin lines and green balls, respectively. One CH_4 molecule is highlighted as a violet large ball, around which other cages are formed and followed by hydrate growth. Hydrate cages are shown as sticks with different colors (green for 5^{12}, blue for $5^{12}6^2$, red for $5^{12}6^3$, orange for $5^{12}6^4$, cyan for $4^15^{10}6^2$, purple for $4^15^{10}6^3$ and pink for $4^15^{10}6^4$). To compare the nucleation processes of CO_2 and CH_4 hydrates, Video S1 and Video S2 were generated with the same time interval.

References

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