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Supplementary Information

Carbon Dioxide Sequestration in Natural Gas Hydrates – Effect of Flue and Noble Gases

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Table S1: Number of molecules in the initial configuration ($t^* = 0$); in seed, $N_{H_2O} = 3450$ and $N_{CH_4} = 600$

System	$N_{CO_2,bulk}$	$N_{G_3,bulk}$	$N_{H_2O,bulk}$	$N_{CH_4,Bulk}$
Pure CH_4	-	-	3440	610
Bulk CO_2	610	-	3440	0
H_2S(3:1)	458	152	3440	0
N_2(3:1)	458	152	3440	0
CO(3:1)	458	152	3440	0
Ne (3:1)	458	152	3440	0
Ar(3:1)	458	152	3440	0
Kr(3:1)	458	152	3440	0
Xe(3:1)	458	152	3440	0
H_2S(1:1)	306	304	3440	0
N_2(1:1)	306	304	3440	0
CO(1:1)	306	304	3440	0
Ne (1:1)	306	304	3440	0
Ar(1:1)	306	304	3440	0
Kr(1:1)	306	304	3440	0
CO_2:Ar(2.35:1.65)	358	252	3440	0
CO_2:Ar(2.5:1.5)	382	228	3440	0
CO_2:Ar(2.5:1.5) (Large)	632	378	5740	0

Table S2: Number of molecules in different systems after NVT simulations at 300K (t^* = 12ns)

System	$N_{CO_2,bulk}$	$N_{G_3,bulk}$	$N_{H_2O,bulk}$	$N_{CH_4,Bulk}$	$N_{H_2O,Seed}$	$N_{CH_4,Seed}$
Pure CH_4	-	-	4296	125	2594	475
Bulk CO_2	563	-	4375	167	2515	433
H_2S(3:1)	433	143	4383	152	2507	448
N_2(3:1)	443	142	4366	144	2524	456
CO(3:1)	441	134	4349	152	2541	448
Ne (3:1)	416	135	4392	169	2498	431
Ar(3:1)	431	129	4373	171	2517	429
Kr(3:1)	431	144	4387	155	2503	445
Xe(3:1)	454	152	4384	128	2506	472
H_2S(1:1)	302	302	4333	150	2557	450
N_2(1:1)	301	300	4321	149	2569	451
CO(1:1)	300	300	4321	147	2569	453
Ne (1:1)	305	291	4383	153	2507	447
Ar(1:1)	303	298	4349	154	2541	446
Kr(1:1)	303	300	4339	147	2551	453
CO_2:Ar(2.35:1.65)	356	244	4359	147	2531	453
CO_2:Ar(2.5:1.5)	380	228	4339	150	2551	450
CO_2:Ar(2.5:1.5) (Large size)	614	363	6676	158	2514	442

Table S3: Box dimensions (Å^3) in different systems at 2ns and 60ns of NPT simulations at 250K and 15MPa. The NPT simulations in larger system size for Ar(2.5:1.5), L(Ar(2.5:1.5)) were simulated for 80ns.

System	Box dimension (Å^3) t = 2ns	Box dimension (Å^3) t = 60ns
Pure CH_4	60.1071 x 60.1071 x 73.3492	59.8692 x 59.8692 x ***73.0590***
Pure CO_2	59.8412 x 59.8412 x 71.7072	59.7240 x 59.7240 x 71.5666
Pure H_2S	59.7444 x 59.7444 x 71.7036	59.6494 x 59.6494 x 71.5896
Bulk CO_2	59.9718 x 59.9718 x 71.7296	59.8384 x 59.8384 x 71.57
H_2S(3:1)	59.9926 x 59.9926 x 72.0016	59.8360 x 59.9926 x 71.8136
N_2(3:1)	59.7720 x 59.7720 x 71.9116	59.7784 x 59.7784 x 71.9192
CO(3:1)	59.8762 x 59.8762 x 71.8618	59.7408 x 59.7408 x 71.6992
H_2S(1:1)	60.1574 x 60.1574 x 72.1994	59.9854 x 59.9854 x 71.9928
N_2(1:1)	59.9402 x 59.9402 x 72.5632	59.7982 x 59.7982 x ***72.3910***
CO(1:1)	59.9992 x 59.9992 x 72.6344	59.9570 x 59.9570 x ***72.5834***
Ne (3:1)	59.7022 x 59.7022 x 71.6528	59.7898 x 59.7898 x 71.7582
Ar(3:1)	59.9840 x 59.9840 x 71.9912	59.9476 x 59.9476 x 71.9476
Kr(3:1)	59.9716 x 59.9716 x 71.9762	59.7680 x 59.7680 x 71.732
Xe(3:1)	60.0512 x 60.0512 x 72.0718	59.7724 x 59.7724 x 71.7372
Ne (1:1)	59.6730 x 59.6730 x 71.6178	59.7186 x 59.7186 x 71.6726
Ar(1:1)	60.1162 x 60.1162 x 72.1496	59.8520 x 59.8520 x 71.8326
Kr(1:1)	60.0788 x 60.0788 x 72.1050	59.9480 x 59.9480 x 71.9478
Ar(2.5:1.5)	60.0644 x 60.0644 x 72.0876	59.8873 x 59.8873 x 71.8750
Ar(2.35:1.65)	59.9294 x 59.9294 x 71.9258	59.8820 x 59.8820 x 71.8686
L(Ar(2.5:1.5))	60.2726 x 60.2726 x 96.436	59.8020 x 59.8020 x 95.6834

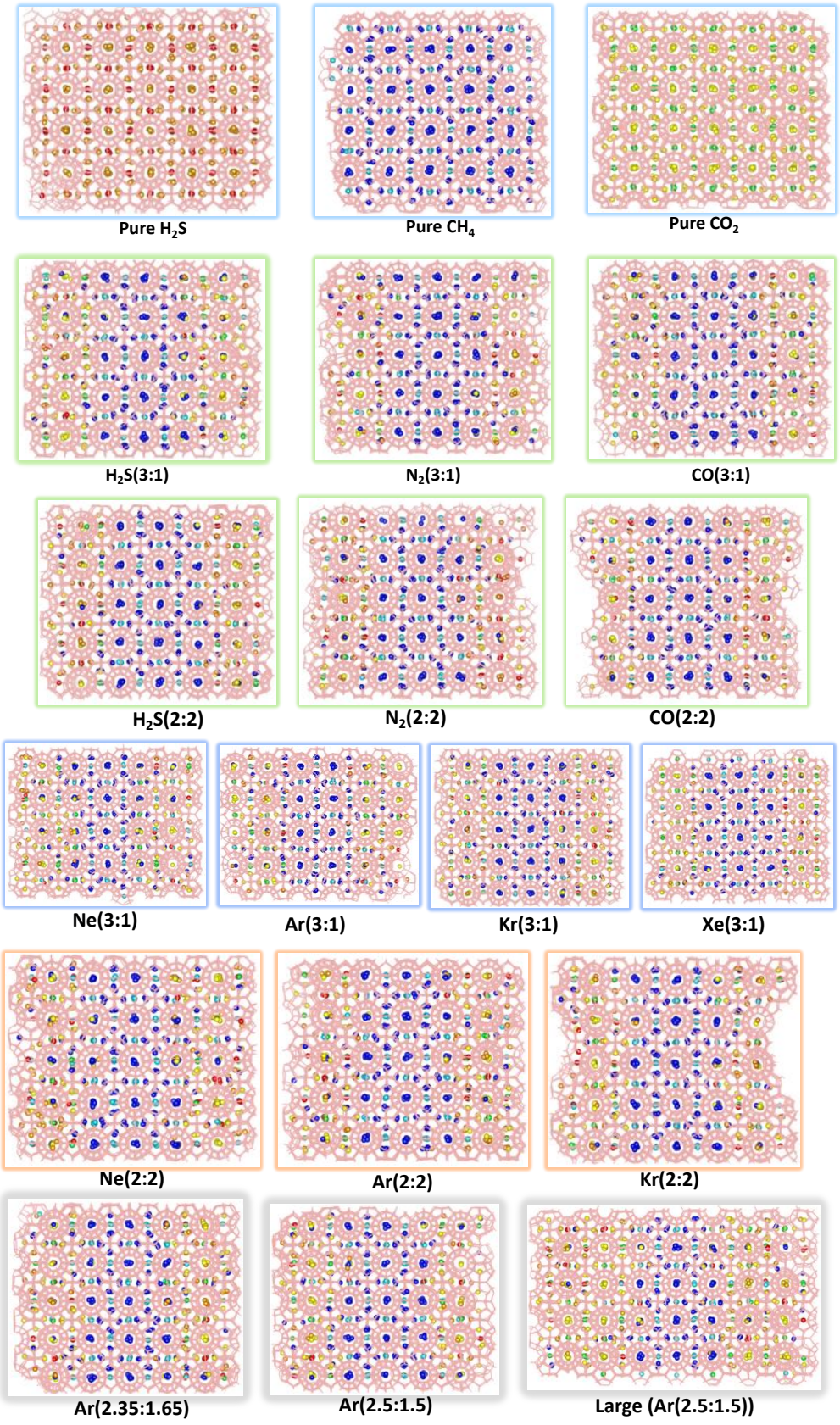

Fig S1: Snapshots of z-axis view of the trajectories of final configurations (60ns, NPT simulation) in different systems; the center of mass of all the gases are shown in the trajectories based on type of cage occupied; cyan (methane in SC), blue (methane in LC), green (carbon dioxide in SC), yellow (carbon dioxide in LC), red (H_2S in SC of pure H_2S system or third gas in SC in third gas systems) and orange (H_2S in LC of pure H_2S system or third gas in LC in third gas systems).

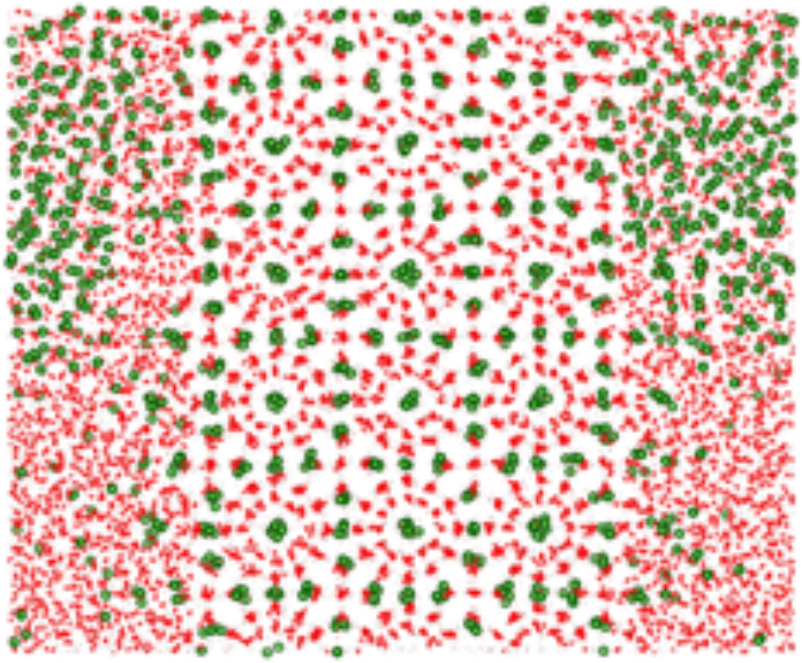

Figure S2: Snapshot of cluster of methane molecule in bulk phase in the final configuration of pure CH_4 system at the end of NVT simulations at 300K; green spheres represent the center of mass of methane molecules.

Table S4: Induction time for formation of first layer besides the interface (Left side of interface, t_{L1} and Right side of interface, t_{R1}). First layer formation time (t_{L1} or t_{R1}) is calculated when F4 OP reaches 0.7 for the Left or Right side first layers; in case of systems that have slightly distorted cages, F4 OP is between 0.69 – 0.70 and F4 OP values for those systems are given in the table and total time t_{tot} (ns) as the time for complete hydrate growth in a system. {Average of t_{L1} and t_{R1} gives t_{ind} (which is reported in Figure 1)}.

System	t_{L1}, ns	t_{R1}, ns	t_{tot} , ns (F4 OP)
$(CH_4)_P$	11.79	12.91	56.69 (0.666)
$(CO_2)_P$	19.10(0.68)	15.56(0.68)	25.39(0.67)
$(H_2S)_P$	5.31	1.79	21.13(0.7)
$(CO_2)_B$	21.570	36.78	48.98(0.698)
H_2S(3:1)	23.48	34.19	58.11(0.699)
N_2(3:1)	29.0	35.0	44.37(0.692)
CO(3:1)	49.0(0.698)	27.0	51.82(0.7)
H_2S(2:2)	14.63	14.16	57.78(0.697)
N_2(2:2)	30.0	49.0	58.56(0.655)
CO(2:2)	39.0	42.0	57.51(0.665)
Ne (3:1)	25.71	40.46(0.67)	41.35(0.694)
Ar(3:1)	36.64	27.86	53.55(0.675)
Kr(3:1)	32.11	13.26	45.05(0.695)
Xe(3:1)	17.23	10.14	29.32(0.70)
Ne (2:2)	34.32	25.20	45.19(0.70)
Ar(2:2)	24.02	25.26	52.08(0.70)
Kr(2:2)	26.06	41.66	50.98(0.68)
Ar(2.5:1.5)	26.83	38.74	57.25(0.665)
Ar(2.35:1.65)	27.40	30.33	57.74(0.68)
L(Ar(2.5:1.5)) 1st layer	21.35	30.20	76.70(0.68)
L(Ar(2.5:1.5)) 2nd layer	54.46	69.49	

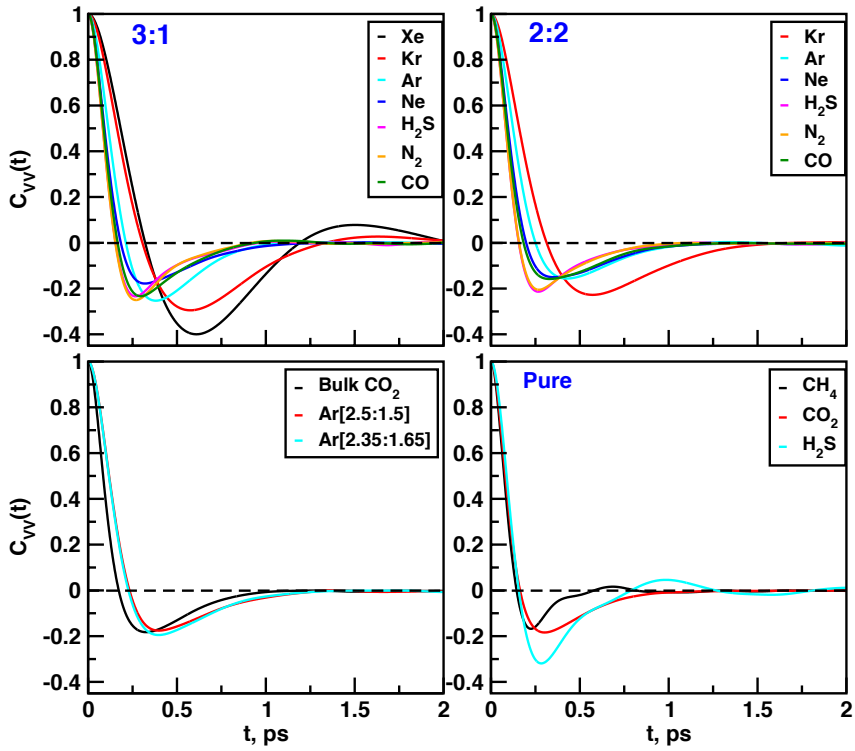

Figure S3: Velocity autocorrelation function plot of gases in different systems at 250K and 15MPa.

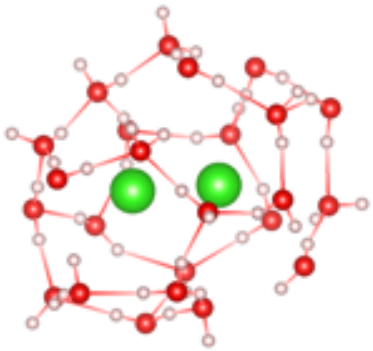

Figure S4: Snapshot of double occupancy of Ne atoms (green sphere) in large cage of hydrate (observed both in Ne(3:1) and Ne(2:2) systems).

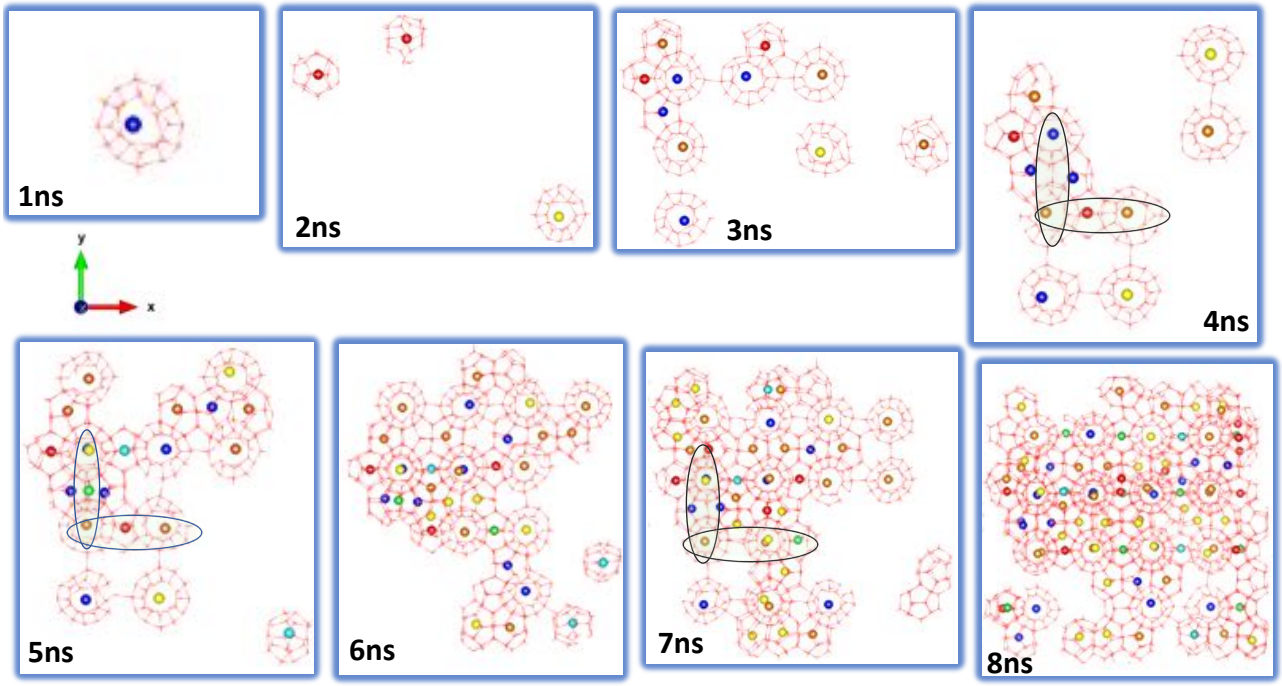

Figure S5: Snapshots of cages formed during NPT simulations in right side of interface in H_2S(2:2) system; cyan, blue, green, yellow, red and orange represent CH_4 in SC, CH_4 in LC, CO_2 in SC, CO_2 in LC, H_2S in SC and H_2S in LC. Large cage of CH_4 formed at 1ns disappears at 2ns; Ovals represent the growth synthon.

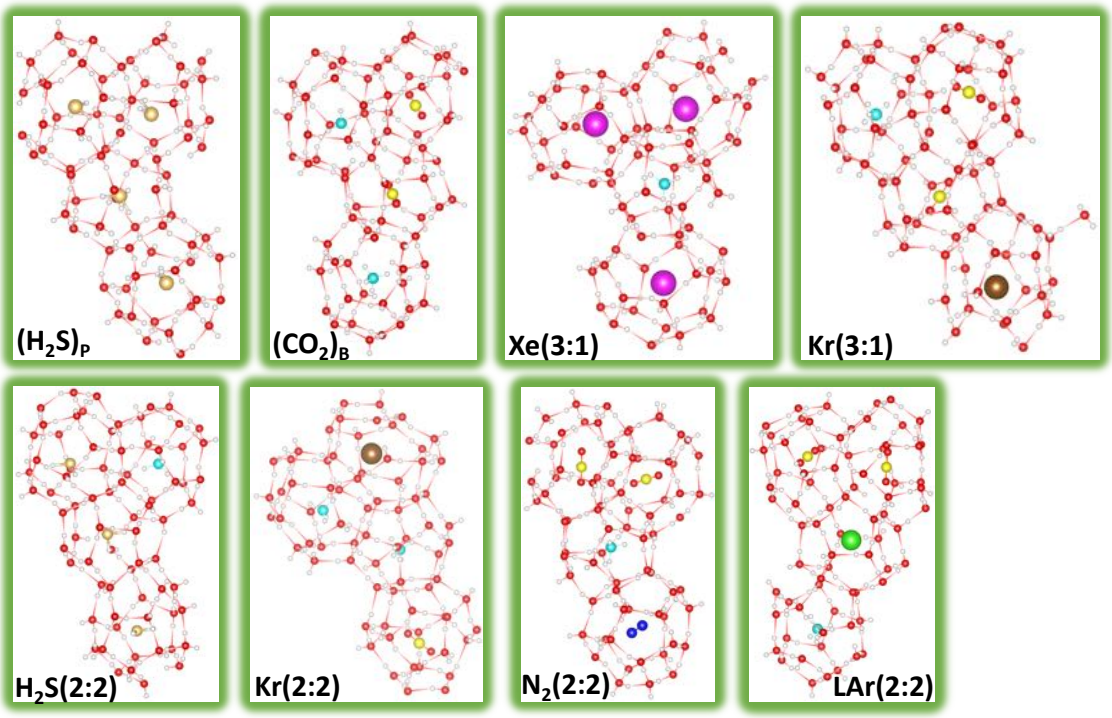

Figure S6: Growth synthon in different systems; here white, red, cyan, magenta, brown, green, yellow, mustard brown and blue spheres represent H, O, C, Xe, Kr, Ar, C(CO_2), S and N.

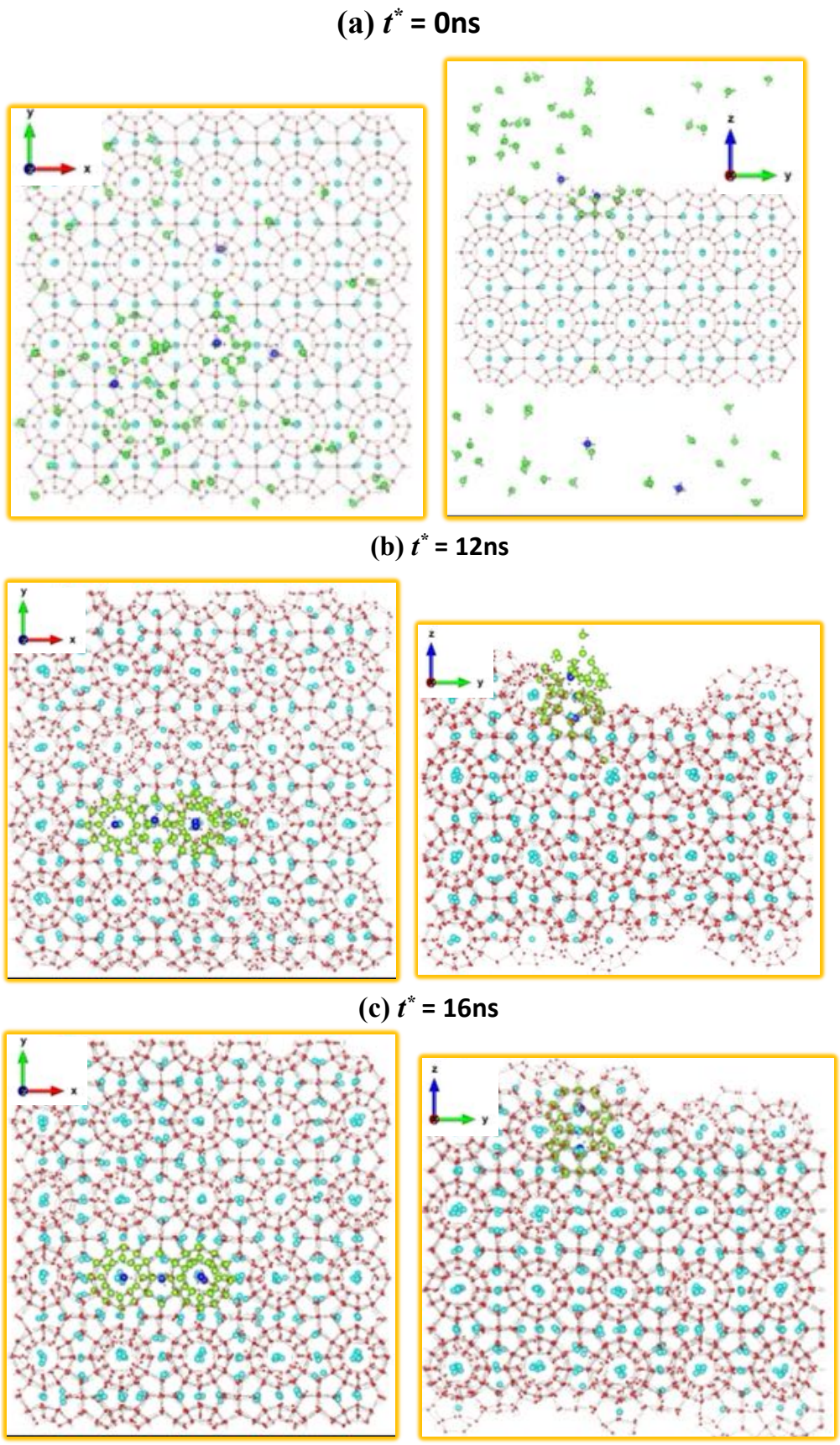

Figure S7: Trajectories of formation of growth synthon in pure CH_4 system at different times, t^* (a) 0ns, (b) 12ns and (c) 16ns (two different views of same trajectory reported for each of the t^*). Red sphere represents oxygen of water molecules that formed cages of hydrate seed at beginning of simulation ($t^* = 0$) and green sphere represents oxygen of water molecules in bulk phase that later form hydrate cage of the growth synthon; similarly cyan sphere represents carbons of methane in hydrate seed in the initial configuration ($t^* = 0$) and dark blue sphere represents methane in the bulk phase that later form the growth synthon.

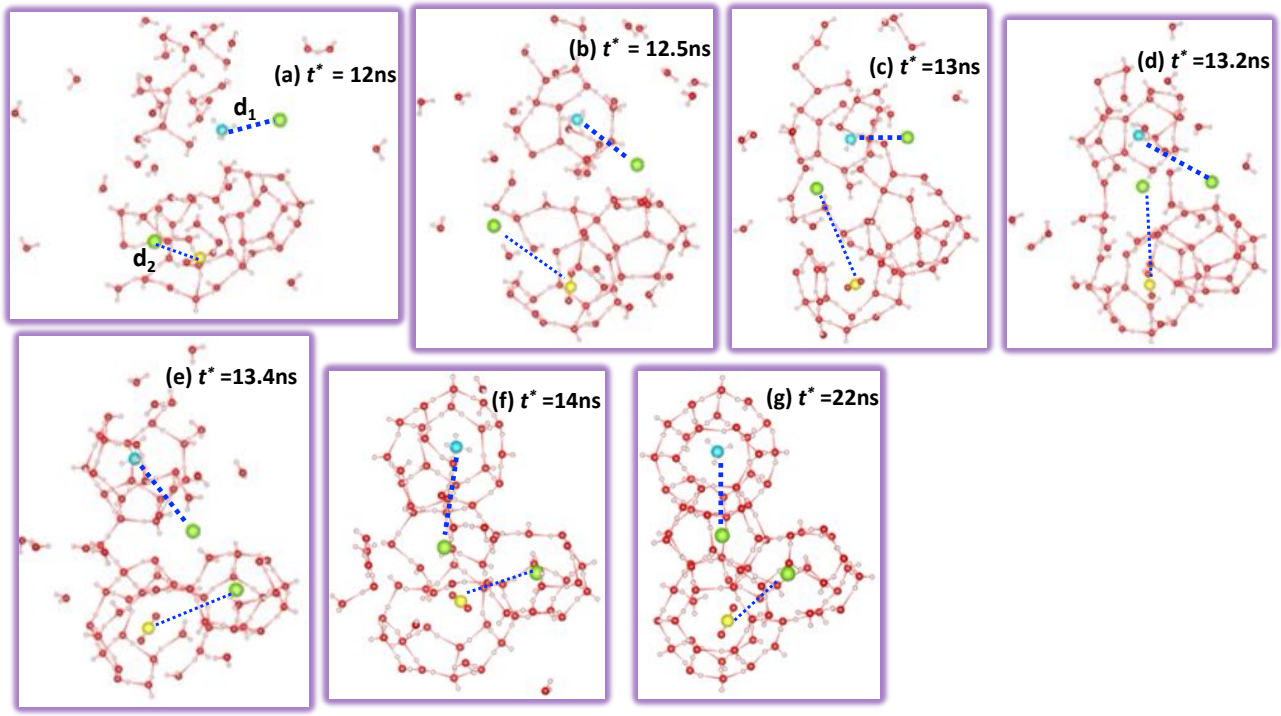

Figure S8: Trajectory of Ar(2:2) system during hydrate growth formation; d_1 and d_2 are distances between gas species that form the growth synthon; (d_1 is distance between CH_4 and Ar) and (d_2 is distance between CO_2 and Ar) respectively where d_1 and d_2 are (a) 6.29 Å and 4.07 Å at t^* = 12ns , (b) 6.79 Å and 4.07 Å at t^* = 12.5ns, (c) 5.8 Å and 9.69 Å at t^* = 13ns, (d) 9.1 Å and 8.96 Å at t^* = 13.2ns, (e) 7.1 Å and 8.39 Å at t^* = 13.4ns, (f) 7.67 Å and 6.79 Å at t^* = 14ns and (g) 6.8 Å and 7.2 Å at t^* = 22ns.

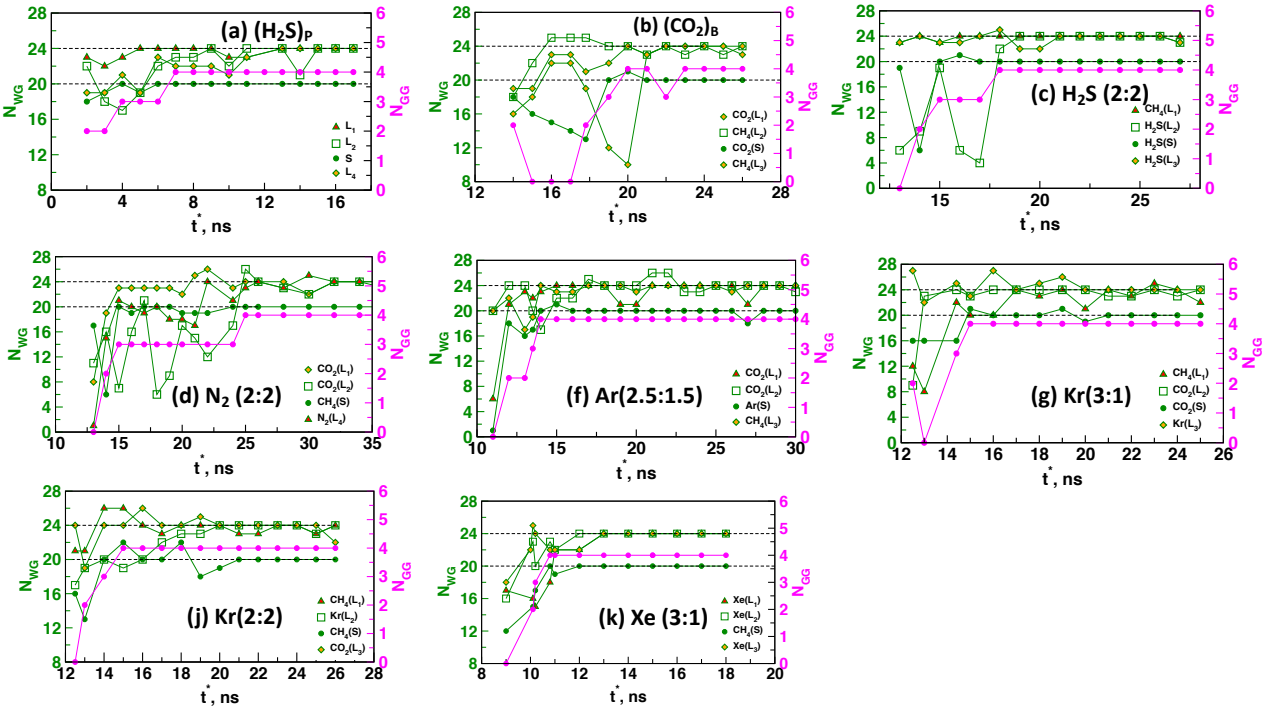

Figure S9: Number of water molecules around a guest (N_{GW}) and number of guest molecules (N_{GG}) within a distance of 8 Å in a growth synthon.

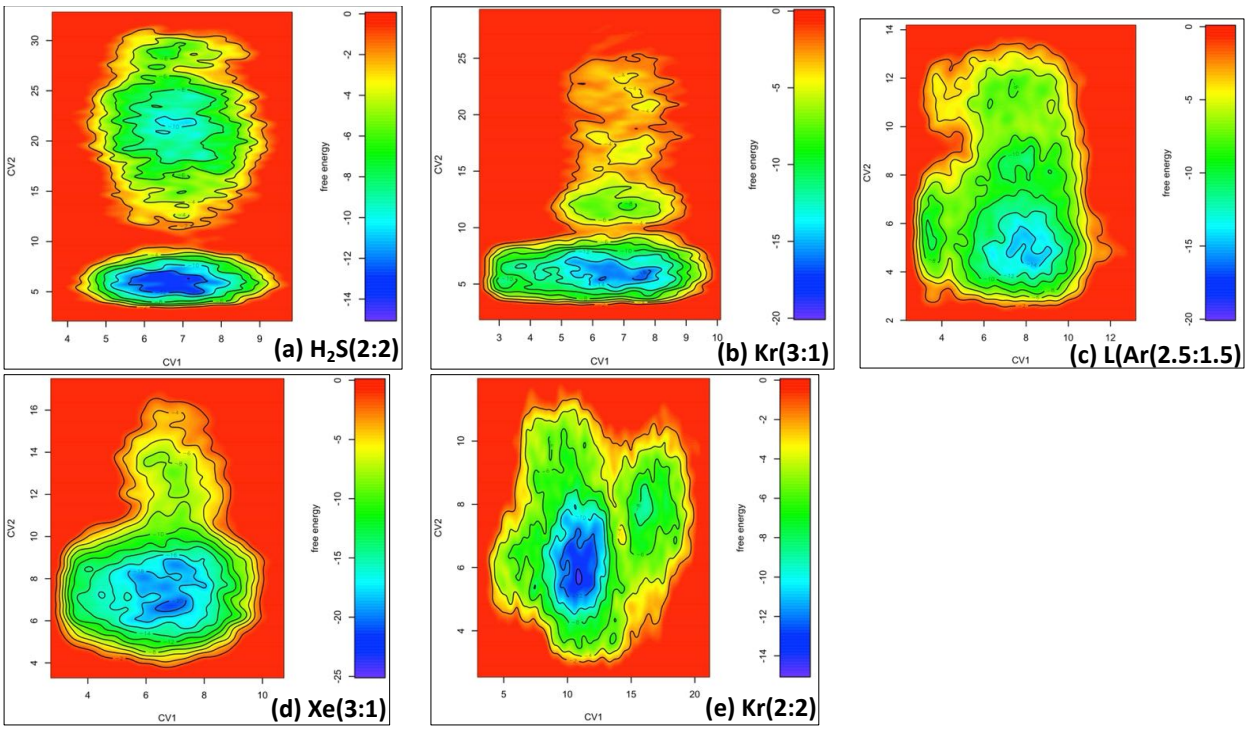

Figure S10: Free energy profiles as a function of collective variable CV1 (distance between guests in SL cage) and CV2 (distance between guests in LL cage).

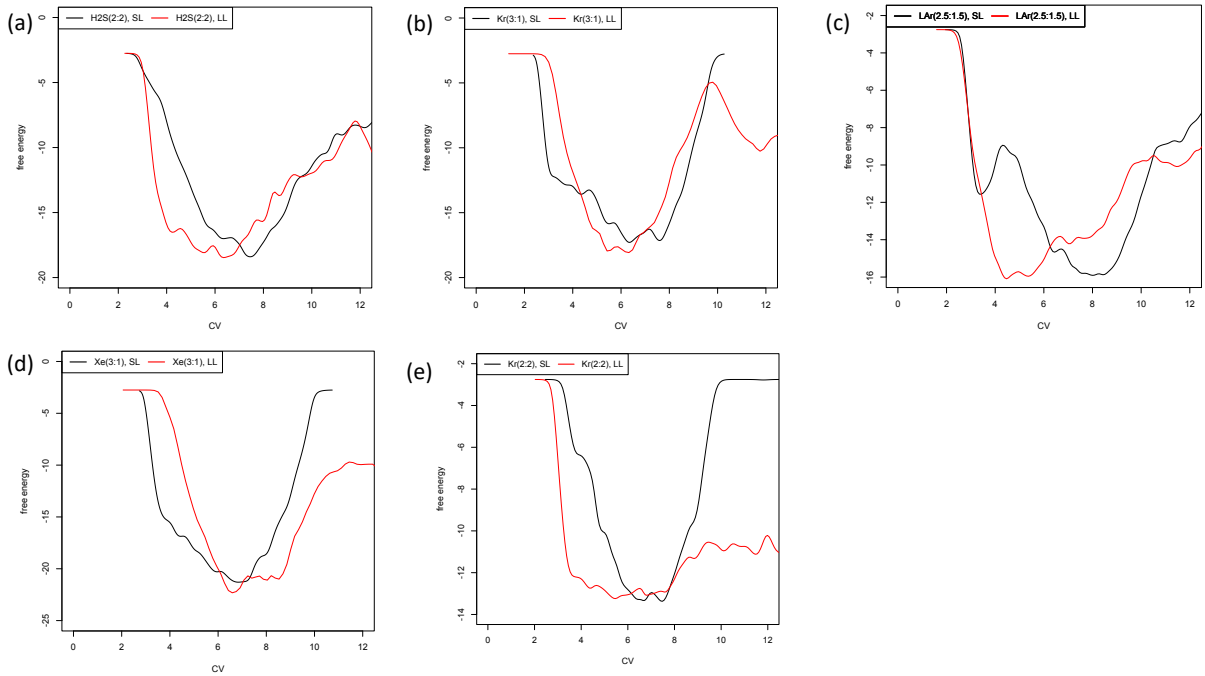

Figure S11: Free energy, kcal/mol *vs* CV1 (distance between two guests in SL cage, Å) or CV2 (distance between two guests in LL cage, Å) in different systems.

Table S5: Zero-point corrected DFT Gibbs Free Energy(ΔG_{DC}) for different combination of gas species in SLDC; SL dual cages (S - small, L - large).

Type (S/L)	CH_4	H_2S	N_2	CO	Ne	Ar	Kr	Xe	CO_2
CH_4	-0.1449	0.3846	7.4484	7.6455	6.2719	7.4886	8.0935	9.7175	2.7120(XY) 4.8725(YZ)
H_2S	-5.6381	-3.4105							-1.3196(P) 1.4251(T)
N_2	1.3617		10.2791						5.8301(P) 6.4871(T)
CO	-0.0169			6.5687(AP) 7.3123(P)					6.6176(P) 5.0564(T)
Ne	5.8565				8.9419				8.6971(XY) 8.1506(YZ)
Ar	6.3202					10.4485			10.9361(XY) 11.5372(YZ)
Kr	5.0526						14.3283		11.3759(XY) 9.3968(YZ)
Xe	8.7649							17.6428	15.2683(XY) 13.4555(YZ)
CO_2	9.8781 (XY) 8.0665 (YZ)	5.7466 (P) 10.0149 (T)	16.8653 (P) 13.7247 (T)	12.5481(P) 14.9320(T)	18.1730 (XY) 17.2694 (YZ)	16.9193 (XY) 16.2661 (YZ)	19.6702 (XY) 17.0071 (YZ)	19.3879 (XY) 16.2221 (YZ)	12.2237(XY) 10.7353(YZ) 10.7472(P)

XY - orientation of molecules represented that both the molecules perpendicular to each other, where large cage guest molecule was parallel to shared pentagonal face, however, small cage guest molecule was perpendicular to shared pentagonal face.

YZ - orientation of molecules represented that both the molecules perpendicular to each other, where, small cage guest molecule was parallel to shared pentagonal face, however, large cage guest molecule was perpendicular to shared pentagonal face.

P - orientation represented that both the molecules were parallel to each other.

T - represented the T shape orientation (perpendicular to each other) of guest molecules, where a guest molecule was parallel to shared pentagonal face, however, other was perpendicular to shared pentagonal face.

AP - represented that both molecules were parallel and opposite in orientation to each other.

Table S6: Zero-point corrected DFT Gibbs Free Energy(ΔG_{DC}) for different combination of gas species in LLDC;

LL dual cages (L - large).

Type (L/L)	CH_4	H_2S	N_2	CO	Ne	Ar	Kr	Xe	CO_2
CH_4	-4.2049	-6.7023	0.8252	-1.4840	2.4428	2.6713	3.8108	5.5145	3.7142(H) 0.3294(T)
H_2S		-8.6702							-0.0734(T) -5.1995(P)
N_2			7.8971						3.3634(P) 7.3888(T)
CO				5.394(P) 4.4339(AP)					4.0179(P) 5.0896(T)
Ne					13.0313				11.6483(H) 9.6742(T)
Ar						12.5563			12.7935(H) 9.7633(T)
Kr							9.6723		11.8692(H) 10.1178(T)
Xe								14.865	12.7552(H) 11.7179(T)
CO_2									6.4482(T) 3.1331(P)

T represents the T shape orientation (perpendicular to each other) of guest molecules, where a guest molecule was parallel to shared hexagonal face, however, other was perpendicular to shared pentagonal face.

H represents the H shape orientation (parallel to each other) of guest molecules, where both the guest molecules were parallel to shared hexagonal face.

P orientation represents that both the molecules were parallel to each other.

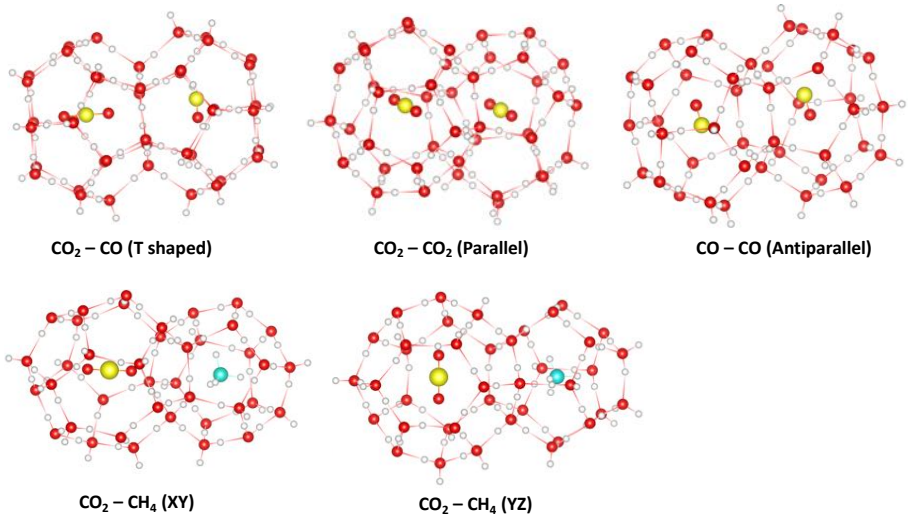

Figure S12: Different orientations chosen for gas species in dual cages for DFT free energy calculations.

LAMMPS Input file for bulk CO_2 system (here User.data file is the configuration file as per LAMMPS format).

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boundary p p p

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        bond_style      harmonic

        angle_style     harmonic

        dihedral_style  none

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0.1546 12.0  10.0

           group H2O type 5 4

kspace_style    pppm/tip4p 1.0e-04

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pair_coeff    2      2     lj/cut/coul/long     0.05590      2.80000
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pair_coeff    4      4    lj/cut/tip4p/long     0.00000      0.00000
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pair_coeff    6      6     lj/cut/coul/long     0.15970      3.02800
pair_coeff    1      2     lj/cut/coul/long     0.06074      3.15000
pair_coeff    1      3     lj/cut/coul/long     0.04450      3.00000
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pair_coeff    1      5     lj/cut/coul/long     0.11056      3.32945
pair_coeff    1      6     lj/cut/coul/long     0.10267      3.26400
pair_coeff    2      3     lj/cut/coul/long     0.04095      2.65000
pair_coeff    2      4     lj/cut/coul/long     0.00000      1.40000
pair_coeff    2      5     lj/cut/coul/long     0.10175      2.97945
pair_coeff    2      6     lj/cut/coul/long     0.09448      2.91400
pair_coeff    3      4     lj/cut/coul/long     0.00000      1.25000
pair_coeff    3      5     lj/cut/coul/long     0.07454      2.82945
pair_coeff    3      6     lj/cut/coul/long     0.06922      2.76400
pair_coeff    4      5    lj/cut/tip4p/long     0.00000      1.57945
pair_coeff    4      6     lj/cut/coul/long     0.00000      1.51400
pair_coeff    5      6     lj/cut/coul/long     0.17198      3.09345
pair_modify tail no

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neigh_modify    delay 0 every 1 check yes

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thermo_style multi

restart 1000 renew

dump    3 all xyz 1000 dump_0.5fs.xyz

min_style sd
minimize 1.0e-8 1.0e-9 100000 1000000

min_style sd
min_modify dmax 0.005
minimize 1.0e-8 1.0e-9 100000 1000000
```

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min_modify dmax 0.005
minimize 1.0e-8 1.0e-9 100000 1000000
min_style sd
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fix 11 all nvt temp 250.0 250.0 60.0
run 2000000
unfix 11

timestep 1.0
fix 11 all nvt temp 300.0 300.0 60.0 #iso 148.038 148.038 2000
run 10000000
```

++++++++++++++++++++++++++++

G09 input file (LLDC with CH_4 as gas species)

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#b3lyp/cc-pVDZ freq

Title Card Required

0 1

O	13.743904	13.765982	13.807000
H	13.413082	12.971174	14.303058
H	14.260877	13.424586	13.030784
O	11.648004	15.247764	12.989533
H	11.688442	15.373376	12.009270
H	12.408649	14.659792	13.240060
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H	8.988419	13.479781	10.230132
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H	14.282026	20.524406	9.003292
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O	11.496015	19.619789	10.284281
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H	10.752567	20.230536	10.039448
O	15.160033	12.944796	11.671477
H	16.032230	13.424005	11.662878
H	15.305515	11.966160	11.664969
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