

Supporting Information

Theoretical Investigation of the Fusion Process of mono-cages to tri-cages with CH₄/C₂H₆ Guest Molecules in sI Hydrates

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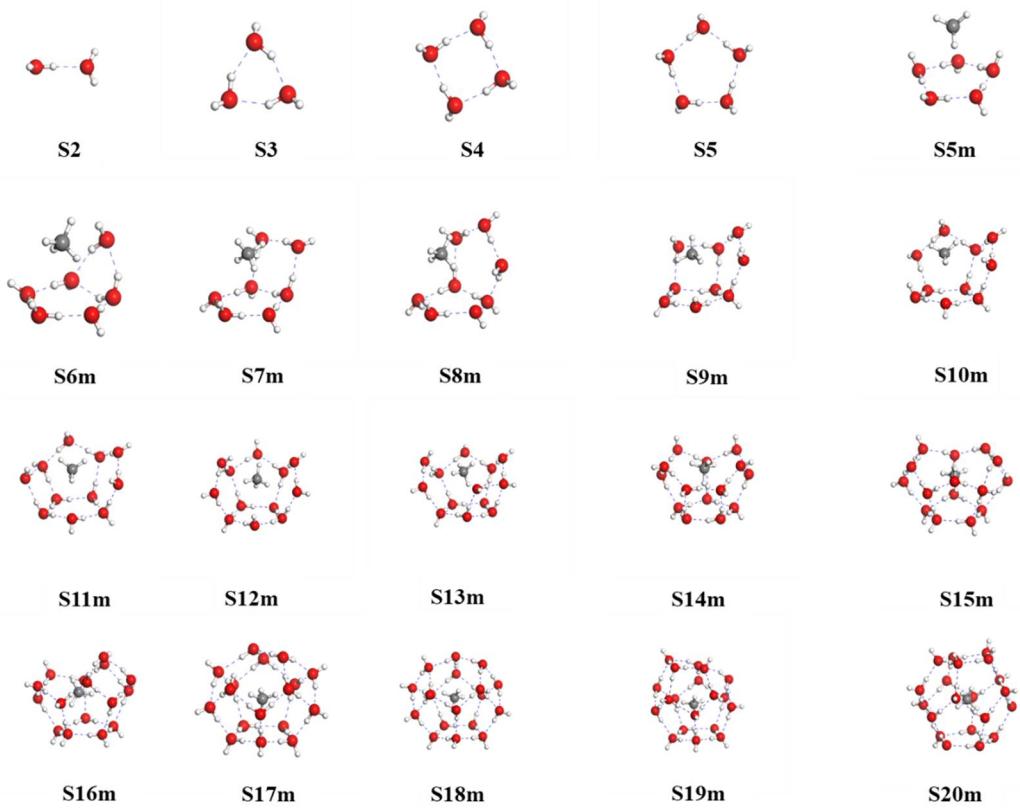


Figure S1. The formation process of small cage in sI hydrate with CH₄ guest molecule (S20m represent small cage, the number of water molecule, and methane guest molecule, respectively).

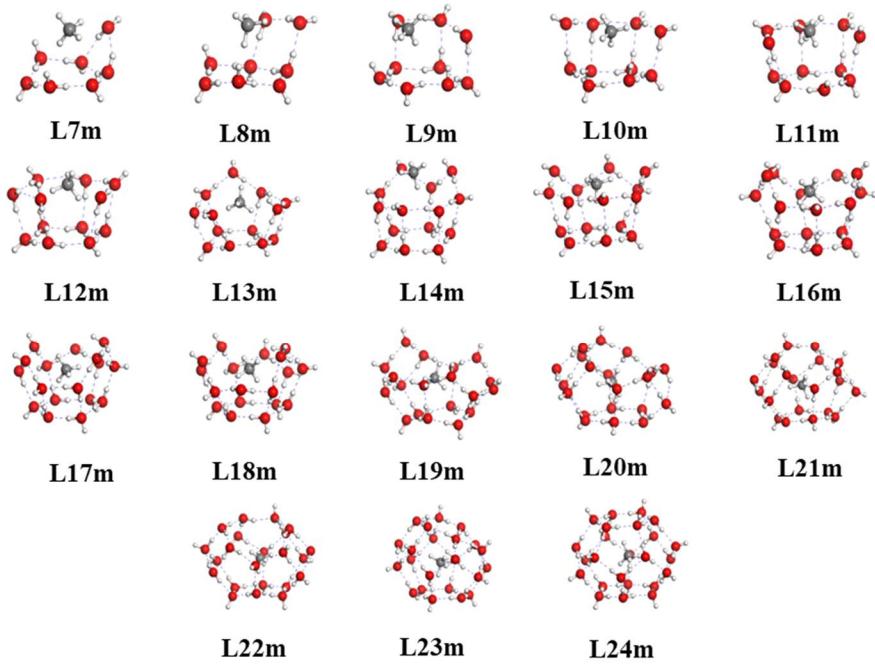


Figure S2. The formation process of large cage in sI hydrate with CH₄ guest molecule (L24m represent large cage, the number of water molecule, and methane guest molecule, respectively).

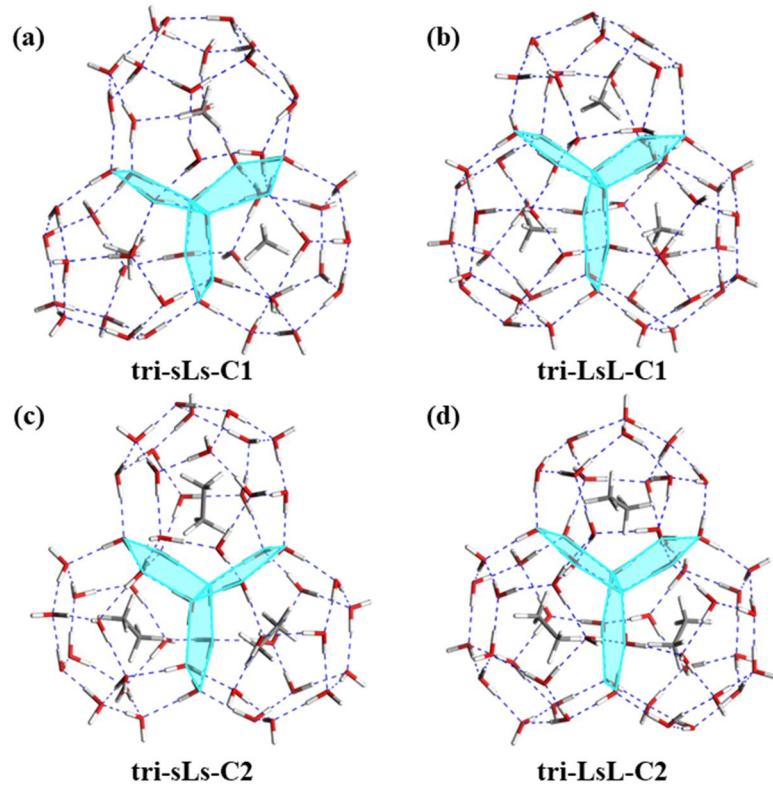


Figure S3. The structural configuration of (a, c) tri-sLs, and (b, d) tri-LsL, shared with three pentagon, and two pentagon and one hexagon water rings, respectively (C1, C2 represent CH₄ and C₂H₆ guest molecule, respectively.).

Table S1. The equilibrium distances of H₂O–guest molecules during the fusion process of mono-cages to tri-cages with different guest molecules. (small-C1 and Large-C1 represent small cage and large cage are occupied by CH₄ guest molecule, and corresponding d_{C-O} is minimum between carbon atom of CH₄ and oxygen atom of H₂O; small-C2 and Large-C2 represent small cage and large cage are occupied by C₂H₆ guest molecule, and corresponding d_{C-O} is minimum between centroid of C₂H₆ and oxygen atom of H₂O.)

Guest molecules	Structure	d _{C-O} (Å)			
		small-C1	small-C2	Large-C1	Large-C2
CH₄	mono-cages	3.684	--	3.809	--
	Double-s	3.604	--	--	--
	Double-Ls	3.385	--	3.744	--
	Double-L	--	--	3.744	--
	tri-LsL	3.325	--	3.684	--
	tri-sLs	3.507	--	3.749	--
C₂H₆	mono-cages	--	3.652	--	3.805
	Double-s	--	3.662	--	--
	Double-Ls	--	3.752	--	3.822
	Double-L	--	--	--	3.822
	tri-LsL	--	3.540	--	3.680
	tri-sLs	--	3.592	--	3.952

	Double-s	3.630	3.706	--	--
	Double-Ls-C1C2	--	3.756	3.724	--
	Double-Ls-C2C1	3.661	--	--	3.783
	Double-L	--	--	3.856	3.908
	tri-LsL-C1C1C2	3.324	--	3.612	3.696
CH₄/C₂H₆	tri-LsL-C1C2C1	--	3.388	3.665	--
	tri-LsL-C1C2C2	--	3.431	3.631	3.664
	tri-LsL-C2C1C2	3.327	--	--	3.625
	tri-sLs-C1C1C2	3.566	3.563	3.721	--
	tri-sLs-C1C2C1	3.563	--	--	3.966
	tri-sLs-C1C2C2	3.598	3.549	--	3.943
	tri-sLs-C2C1C2	--	3.576	3.717	--

Table S2. The stabilization energy (E_{sta} , kJ/mol), stabilization energy per H_2O molecule ($E_{\text{sta-p}}$, kJ/mol), and capture energy (E_c , kJ/mol) of capturing guest molecules $\text{CH}_4/\text{C}_2\text{H}_6$ one by one in double cages structure (For example, s-1C1 means the small cage of empty double cages captures CH_4 , and sL-C1C2 means the large cage of half-full double cages captures C_2H_6 based on small cage capturing CH_4).

Guest molecule	Structure	E_{sta}	$E_{\text{sta-p}}$	E_c
CH_4	Double-s	s-1C1	1751.68	50.05
		s-2C1	1780.12	50.86
	Double-Ls	s-1C1	2116.83	54.28
		L-1C1	2115.38	54.24
		sL-2C1	2141.74	54.92
	Double-L	Ls-2C1	2141.74	54.92
		L-1C1	2313.97	55.09
		L-2C1	2339.38	55.70
C_2H_6	Double-s	s-1C2	1756.82	50.19
		s-2C2	1789.15	51.12
	Double-Ls	s-1C2	2115.80	54.25
		L-1C2	2126.62	54.53
		sL-2C2	2152.63	55.20
	Double-L	Ls-2C2	2152.63	55.20
		L-1C2	2326.60	55.40
		L-2C2	2364.07	56.29

	s-C1	1751.68	50.05	-26.98
	s-C1C2	1783.62	50.96	-31.94
	Double-s			
	s-C2	1756.82	50.19	-32.12
	s-C2C1	1783.62	50.96	-26.80
CH₄/C₂H₆	s-C1	2116.83	54.28	-26.17
	s-C2	2115.80	54.25	-25.14
	L-C1	2115.38	54.24	-24.73
	L-C2	2126.62	54.53	-35.96
	Double-Ls			
	sL-C1C2	2153.12	55.21	-36.29
	sL-C2C1	2140.82	54.89	-25.02
	Ls-C1C2	2140.82	54.89	-25.44
	Ls-C2C1	2153.12	55.21	-26.50
Double-L	L-C1	2313.97	55.09	-24.22
	L-C1C2	2351.56	55.99	-37.59
	L-C2	2326.60	55.40	-36.85
	L-C2C1	2351.56	55.99	-24.96