Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information for

Clathrate Ice sL: A New Crystalline Phase of Ice with Ultralow Density Predicted by First-principles Phase Diagram Computations

Yuan Liu*[,a,b] and Lars Ojamäe[b]

[a]*Beijing Advanced Innovation Center for Soft Matter Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China.*

[b]*Department of Chemistry, IFM, Linköping University, SE-58 183 Linköping, Sweden.*

**e-mail: yuanliu@mail.buct.edu.cn*

Table S1. The coordinates of the new phase sL of clathrate ice from DFT vdW-DF2 optimization. (a=b=c=10.7117Å, α=β=γ=90°)

Atom	X (Å)	Y (Å)	Z (Å)
O	0.070906	1.996996	3.914729
O	0.060685	8.725550	3.954985
O	0.002263	1.963960	6.725992
O	-0.051950	8.690175	6.762254
O	3.997089	-0.045360	1.999131
O	3.951763	-0.081500	8.734746
O	6.805082	0.052579	2.020671
O	6.760745	-0.020750	8.756235
O	1.993875	3.926125	-0.027960
O	8.716213	3.961885	-0.068450
O	1.972617	6.728908	-0.059720
O	8.689525	6.757085	0.047342
O	1.999243	-0.038460	6.763813
O	8.718122	-0.016700	6.794328
O	2.043158	-0.006130	3.956348
O	8.762810	-0.019570	3.988162
O	0.055150	3.926022	8.677452
O	-0.037970	3.971367	1.962337
O	-0.057520	6.720022	8.706833
O	-0.004770	6.775448	1.982688
O	3.958283	1.966267	0.011593
O	3.930891	8.692012	-0.002060
O	6.764513	2.002943	-0.004610
O	6.738515	8.724037	0.025506
H	-0.717910	1.413794	3.789174
H	-0.000300	2.738237	3.260317
H	0.834781	9.342148	3.871031
H	0.021053	8.495116	4.917089
H	0.033553	2.189272	5.762223
H	-0.783040	1.364203	6.824215
H	-0.031930	7.948613	7.420462
H	0.747112	9.251829	6.912563
H	4.961930	-0.010230	2.219396
H	3.896368	-0.827580	1.395923
H	3.819291	0.713548	9.307537
H	3.292787	-0.032010	7.995306
H	7.463510	-0.005280	2.759820
H	6.930583	-0.743620	1.447936
H	6.855805	0.762885	9.358990
H	5.796978	-0.052380	8.531447
H	1.408096	3.801140	0.758410
H	2.728743	3.263202	0.031491
H	9.339570	3.865241	-0.834700
H	8.493657	4.926296	-0.038070
H	1.334933	6.828636	-0.811880
H	2.194591	5.763717	-0.049610
H	7.958601	7.426725	0.063395
H	9.265434	6.907920	0.837815
H	2.233705	-0.053430	5.801943
H	1.376820	0.728921	6.848443
H	9.276905	-0.820080	6.943724
H	7.980559	-0.032710	7.456998
H	1.484947	0.795493	3.797408
H	2.779973	-0.001830	3.292728
H	9.385156	-0.786520	3.899092
H	8.531809	-0.001450	4.951075
H	0.062596	3.257173	7.945451
H	0.845483	3.767360	9.251196
H	-0.023870	4.936305	2.185247
H	-0.791170	3.876645	1.325273
H	-0.030280	5.755875	8.482218
H	-0.819540	6.817190	9.335288
H	0.778728	6.900930	1.393251
H	0.060832	7.435178	2.720028
H	3.878231	1.340646	0.776855
H	4.920838	2.197641	-0.014330
H	3.270904	7.953253	-0.045130
H	3.791894	9.261630	-0.800180
H	6.927867	1.454900	0.802887
H	7.428153	2.739847	-0.013560
H	6.832787	9.334379	-0.750310
H	5.774850	8.495954	0.041413

Table S2. Structural and energetic parameters of ice XI and clathrate ice sL and sIII calculated by functional vdW-DF2, SCAN, and PBE.

Phase	**Ice XI**				**sL**			**sIII**		
	Expt.	vdW-DF2	SCAN	PBE	vdW-DF2	SCAN	PBE	vdW-DF2	SCAN	PBE
N		8	8	8	24	24	24	48	48	48
V_{cell} **(Å^3)**	257[a]	262	233	242	1229	1087	1126	2486	2180	2263
ρ (g/cm^3)	0.93[a]	0.913	1.026	0.988	0.584	0.66	0.637	0.577	0.658	0.634
E_{latt} **(kJ/mol)**	−58.99[b]	−63.61	−69.48	−64.31	−56.90	−63.46	−57.86	−56.30	−63.02	−57.03

[a]Ref. 25 [b]Ref. 26 and 27.

Table S3. The maximum, minimum, and average O-O, O-H, and H…O distances of nearest-neighbor in ice XI and various clathrate ices.

Phase		Ice XI	sI	sII	sII[a]	sH	sK	sL	sL_I	sL_II	sIII
d_{OO} (Å)	max	2.774	2.815	2.810	2.804	2.808	2.861	2.845	2.798	2.857	2.822
	min	2.770	2.759	2.753	2.767	2.764	2.737	2.766	2.789	2.759	2.787
	average	2.772	2.784	2.783	2.785	2.785	2.785	2.797	2.794	2.790	2.799
d_{OH} (Å)	max	0.995	0.995	0.995	0.996	0.995	0.996	0.993	0.993	0.994	0.991
	min	0.994	0.992	0.993	0.993	0.992	0.990	0.988	0.992	0.987	0.989
	average	0.995	0.994	0.994	0.994	0.994	0.994	0.991	0.993	0.992	0.990
$D_{H\cdots O}$ (Å)	max	1.780	1.825	1.818	1.812	1.821	1.871	1.889	1.817	1.917	1.864
	min	1.778	1.764	1.759	1.773	1.774	1.742	1.776	1.810	1.765	1.810
	average	1.779	1.792	1.791	1.793	1.794	1.793	1.828	1.814	1.812	1.828

[a]primitive cell of sII.

Table S4. Adsorption energies (E_{ads}) of various numbers of hydrogen molecules encapsulated in the small ($4^6 6^8$) and large ($4^{12} 6^8 8^6$) cavities of clathrate ice sL.

N in $4^6 6^8$ cavity	1	2	3	4	5	6	7	8
$\boldsymbol{E_{ads}}$ (kJ/mol)	−9.55	−10.05	−9.14	−6.86	−5.07	−5.13	−3.85	−2.84
N in $4^{12} 6^8 8^6$ cavity	1	2	4	8	12	15	16	17
$\boldsymbol{E_{ads}}$ (kJ/mol)	−7.65	−7.66	−7.67	−7.97	−8.13	−8.16	−8.19	−8.13
N in $4^{12} 6^8 8^6$ cavity	20	24	28	32	36	40	–	–
$\boldsymbol{E_{ads}}$ (kJ/mol)	−7.76	−7.15	−6.15	−5.31	−4.34	−3.36	–	–

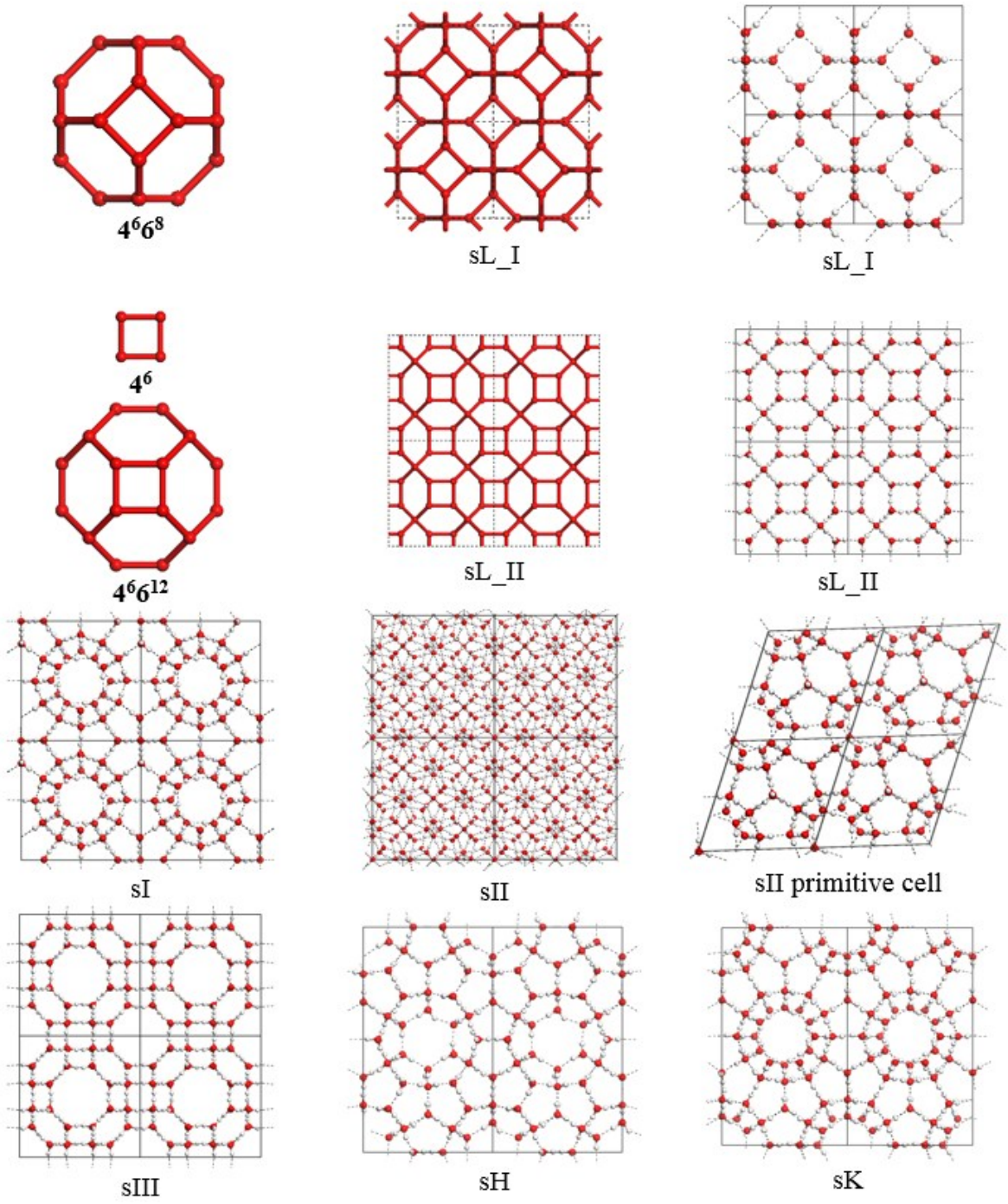

Figure S1. Crystal structures of various clathrate ices, 2×2 unit cells for sL_I, sL_II, sI, sII, sII primitive cell, and sIII, 2×1 unit cells for sH and sK. Note: the red balls represent oxygen atoms, white balls represent hydrogen atoms. 4^x6^y means the cage is made up of x four- and y six-membered rings.

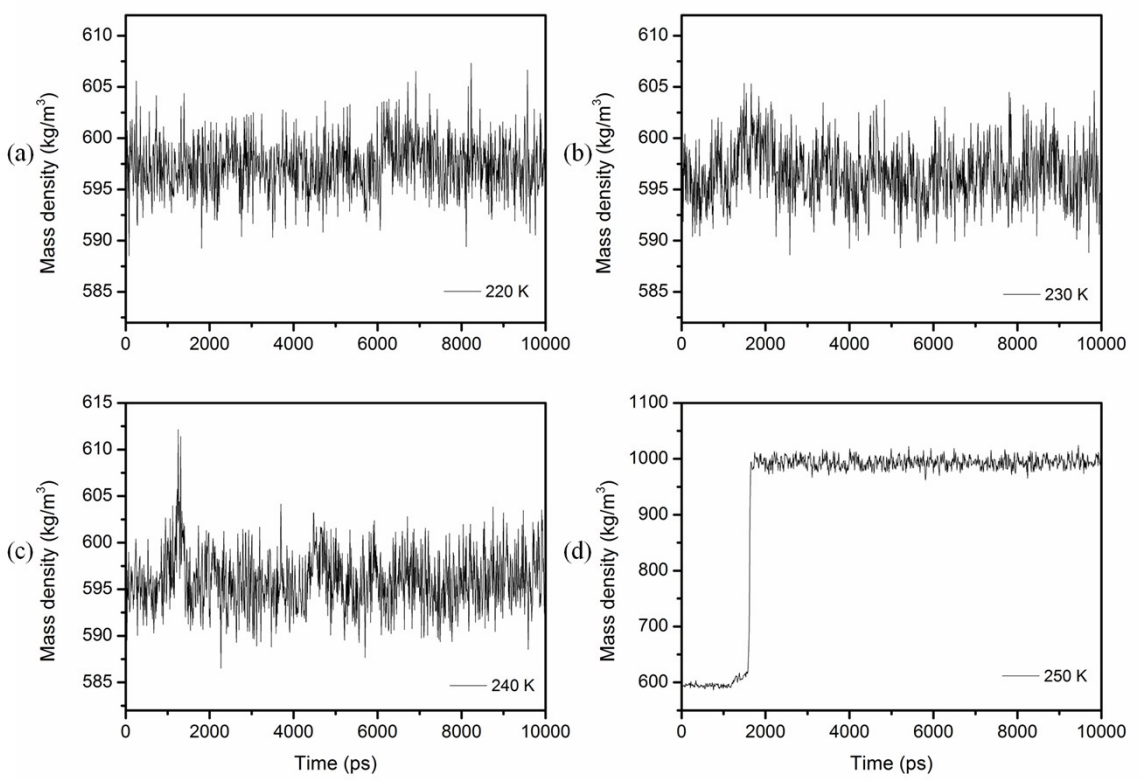

Figure S2. Mass density of clathrate ice sL as a function of time at temperature (a) 220 K, (b) 230 K, (c) 240 K, and (d) 250 K by TIP4P/2005 NPT simulations in Gromacs.

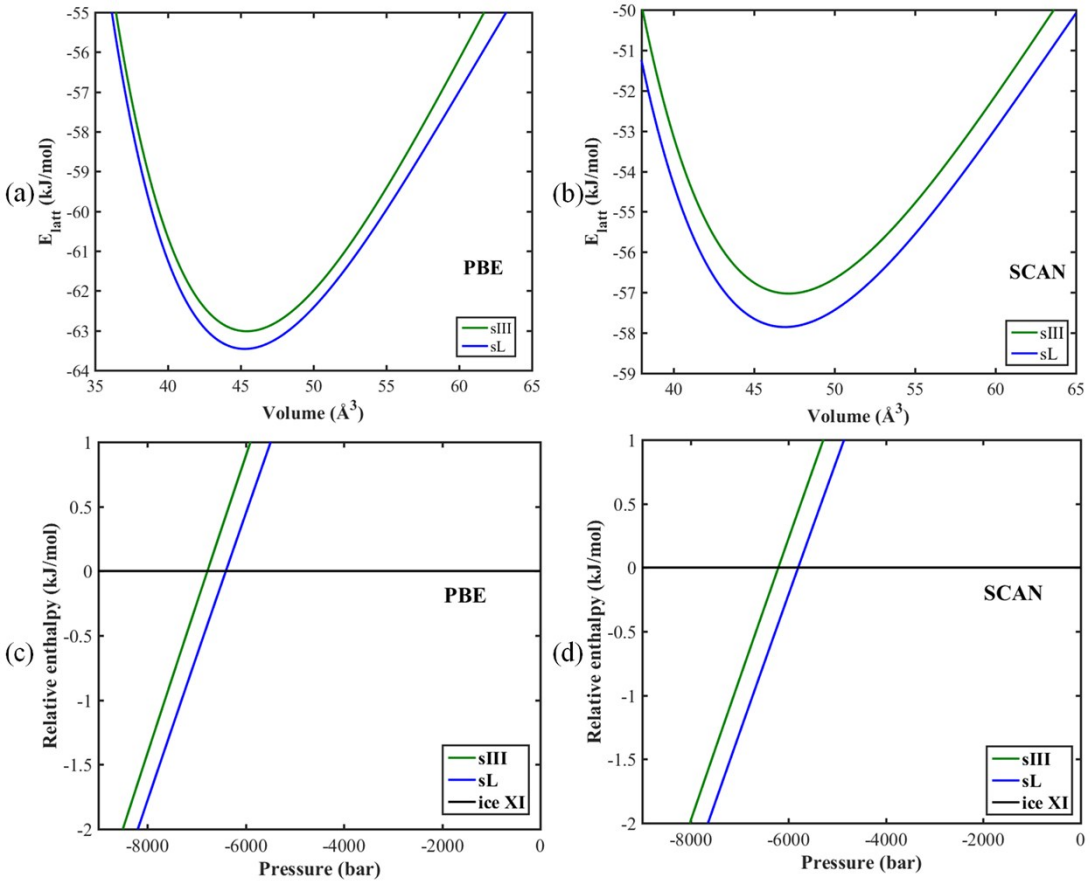

Figure S3. Lattice energies (E_{latt}) of clathrate ice sL and sIII as function of volume per water molecule by (a) PBE and (b) SCAN functionals, and relative enthalpy per molecule at 0K as a function of the pressure for clathrate ice sL and sIII with ice XI as a reference by (c) PBE and (d) SCAN functionals.