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Supplementary Materials for

A new phase diagram of water under negative pressure: The rise of the lowest-density clathrate s-III

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The PDF file includes:

Table S1. Fractional coordinates of the structure III (s-III) clathrate with cubic lattice (space group: $P\bar{4}3n$, lattice constant: 13.431 Å) from vdW-DF2 DFT calculation.

Atom	*X*	*Y*	*Z*	Occupancy
O	0.74614	0.09977	0.60926	1.0
O	0.59947	0.10939	0.75379	1.0
H	0.69099	0.11146	0.65675	1.0
H	0.76134	0.02799	0.61380	1.0
H	0.61120	0.15692	0.80890	1.0
H	0.52764	0.11385	0.73868	1.0

Table S2. Average lengths of O–H covalent bond ($d_{O–H}$) and hydrogen bond ($d_{O\cdots H}$) for different phases (ices XI, ice *i*, s-I, s-II, s-H, SGT, s-K, s-T, and s-III clathrates) based on vdW-DF2 DFT computation.

Phase	Ice		Clathrate						
	XI	*i*	s-I	s-K	s-II	s-T	s-H	SGT	s-III
d_{O-H} (Å)	0.995	0.995	0.995	0.995	0.995	0.995	0.995	0.995	0.995
$d_{O\cdots H}$ (Å)	1.795	1.795	1.775	1.775	1.775	1.805	1.795	1.595	1.795

Table S3. Mass density (ρ) and lattice cohesive energy per water molecule (E_{latt}) for different phases (ice XI, ice *i*, s-I, s-II, s-H, SGT, s-K, s-T, and s-III clathrates) based on vdW-DF2 (DFT) optimization, and another independent optimization using the TIP4P/2005 water model (at zero temperature and zero pressure).

	Method	Ice		Clathrate						
		XI	*i*	s-I	s-K	s-II	s-T	s-H	SGT	s-III
ρ (g/cm^3)	vdW-DF2	0.900	0.855	0.813	0.808	0.804	0.792	0.768	0.722	0.593
	TIP4P/2005	0.969	0.897	0.842	0.841	0.830	0.839	0.811	0.771	0.605
E_{latt} (kJ/mol)	vdW-DF2	62.840	61.310	61.38	60.76	61.37	60.23	60.79	59.27	55.77
	TIP4P/2005	63.100	61.580	62.02	61.58	61.96	61.13	61.60	60.36	57.27

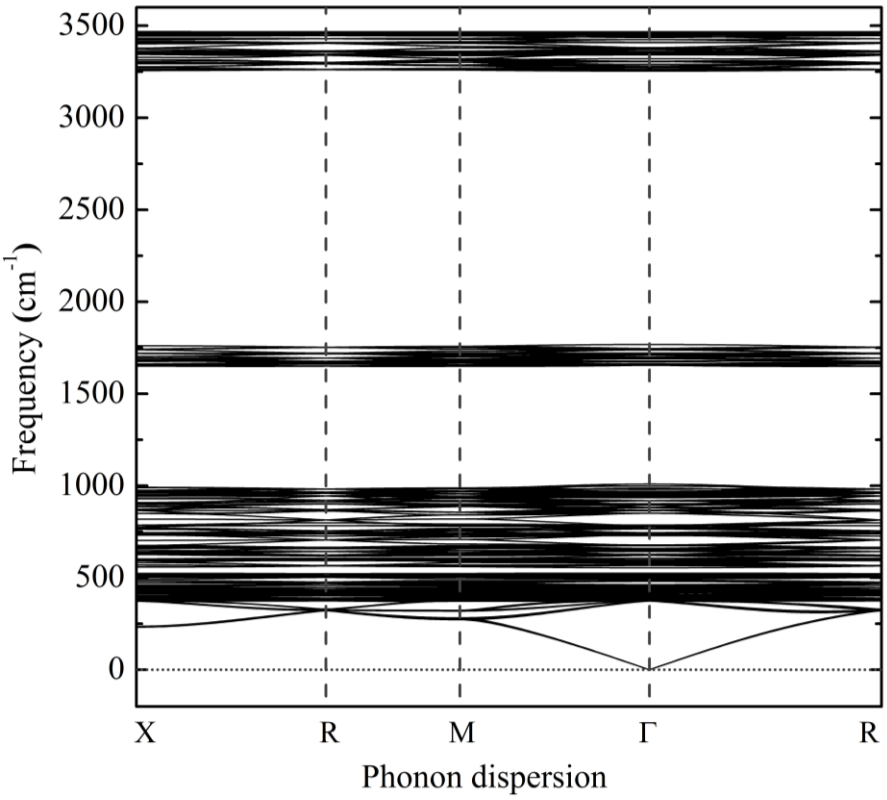

Figure S1. Phonon dispersion for guest-free s-III ice clathrate based on vdW-DF2 DFT computation. Definition of special points in the Brillouin zone: X - (0.5, 0.0, 0.0), R - (0.5, 0.5, 0.5), M - (0.5, 0.5, 0.0), Γ- (0.0, 0.0, 0.0).

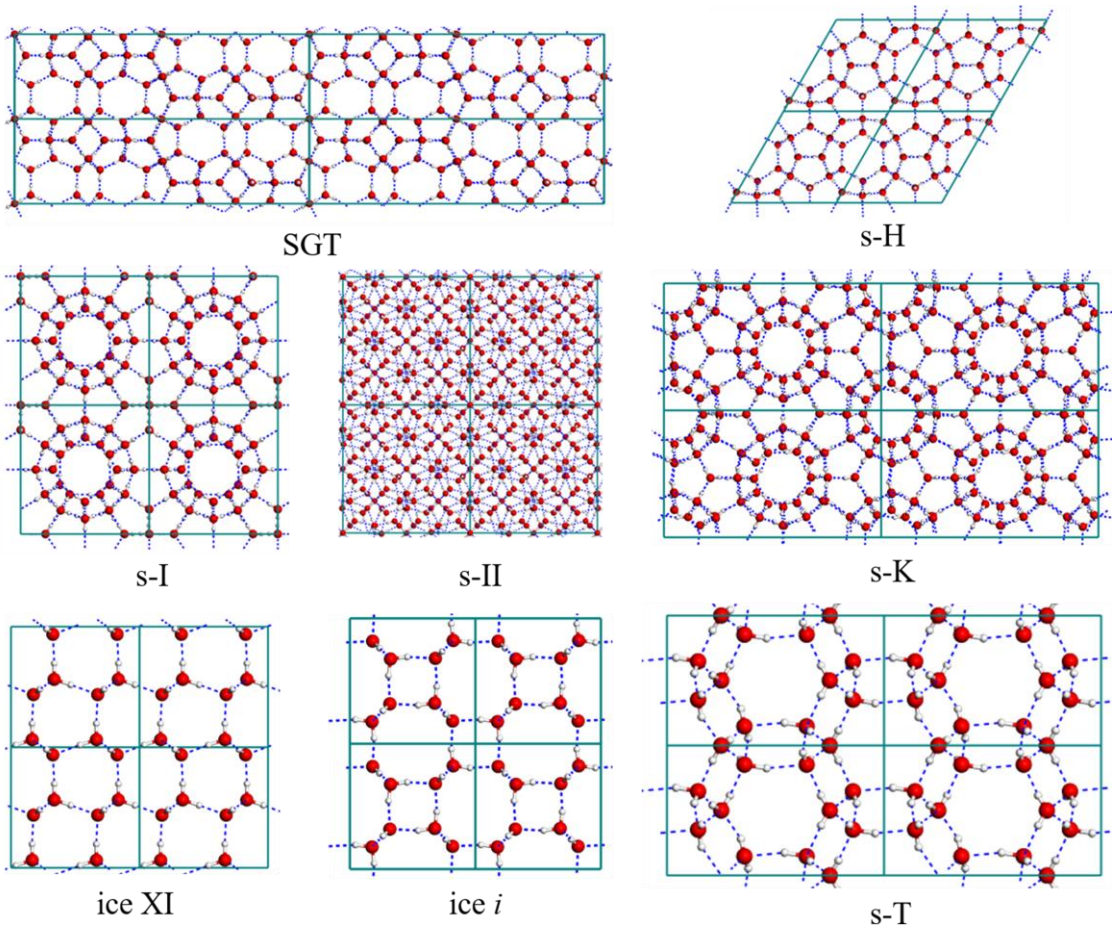

Figure S2. Crystal structures (2 × 2 unit cells) of ice *i*, ice XI, and clathrates of s-T, s-I, s-II, s-K, SGT, and s-H phases (blue dash lines for hydrogen bonds, red for oxygen, and white for hydrogen).

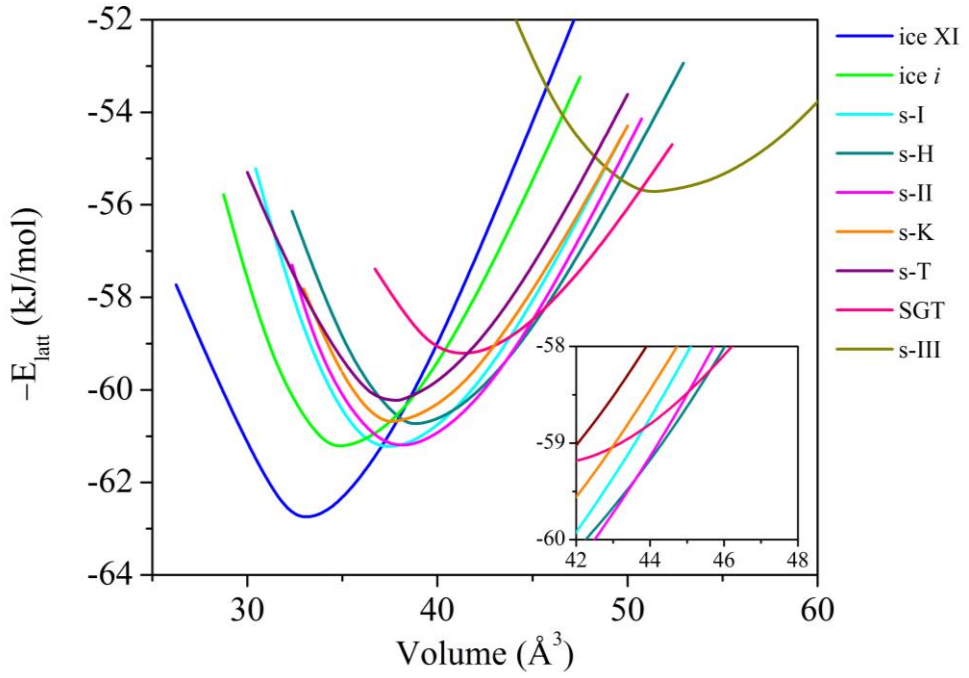

Figure S3. Lattice cohesive energies (E_{latt}) for structures ice XI, ice *i*, s-K, s-I, s-II, s-H, s-III, SGT, and s-T clathrates as function of volume per water molecule. Inset is amplification of the region for the volume between 42 Å^3 and 48 Å^3. E_{latt} is defined as: $E_{latt} = E_w - E_{cry}/N$, where N is the number of water molecules in the crystal, E_{cry} and E_w are the total energies of the ice/clathrate crystal and an individual water molecule, respectively. We also considered the ice *i′* (*13*) and ice 0 (*5*) polymorphs, which are not shown in this Figure for a clear view, since the curve of ice *i′* basically overlaps with ice *i* and the entire energy-volume curve of ice 0 is higher than that of the reference ice XI.

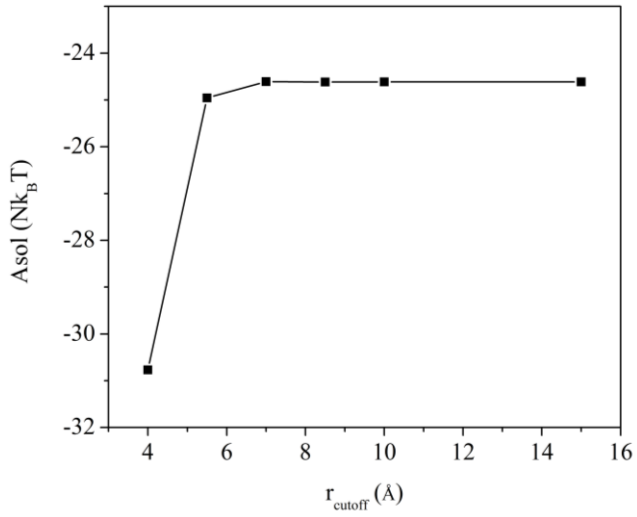

Figure S4. Computed Helmholtz energy (A_{sol}) of the s-III clathrate based on the TIP4P/2005 potential, using the Einstein method, as a function of real-space cutoff distance r_{cutoff}. In the simulations, the thermodynamic conditions are 200 K and 1 bar.