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

Supporting Information

Phase Diagram of Water-Methane by First-Principles Thermodynamics: Discovery of MH-IV and MH-V Hydrates

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Table S1. Fractional coordinates of the MH-IV hydrate orthogonal lattice (space group: *Iba2*, lattice constant: a = 8.948 Å, b = 8.987 Å, c = 7.381 Å) from vdW-DF2 DFT calculation.

Atom	*X*	*Y*	*Z*	Occupancy
H	0.27266	1.22508	0.93907	1.0
H	0.34775	1.15193	0.11343	1.0
H	0.90464	0.97206	0.59901	1.0
H	0.97176	1.09495	0.76993	1.0
H	0.33802	0.96197	0.89646	1.0
H	0.46205	0.83903	0.89764	1.0
O	0.34800	1.15112	0.97911	1.0
O	0.35819	0.85839	0.85704	1.0
C	1.00000	1.00000	0.68450	1.0

Table S2. Fractional coordinates of the MH-V with monoclinic lattice (space group: $P2_1/c$, lattice constant: a = 11.285 Å, b = 8.877 Å, c = 9.048 Å)) from vdW-DF2 DFT calculation.

Atom	*X*	*Y*	*Z*	Occupancy
H	0.79041	0.54643	0.80364	1.0
H	0.75741	0.66954	0.6509	1.0
H	0.84386	0.51612	1.30487	1.0
H	0.72305	0.4916	1.02144	1.0
H	0.92699	0.601	1.2185	1.0
H	0.93804	0.40203	1.25169	1.0
H	0.29098	0.27988	0.65586	1.0
H	0.46607	0.27476	0.72497	1.0
H	0.35599	0.54464	0.64397	1.0
H	0.27843	0.66213	1.45588	1.0
H	0.0546	0.67055	1.04767	1.0
H	0.24257	0.7297	1.16341	1.0
O	0.80635	0.65523	0.79846	1.0
O	0.35469	0.33548	0.63656	1.0
O	0.33857	0.65376	0.61072	1.0
O	0.18838	0.65959	1.18493	1.0
C	0.85791	0.50276	1.19903	1.0

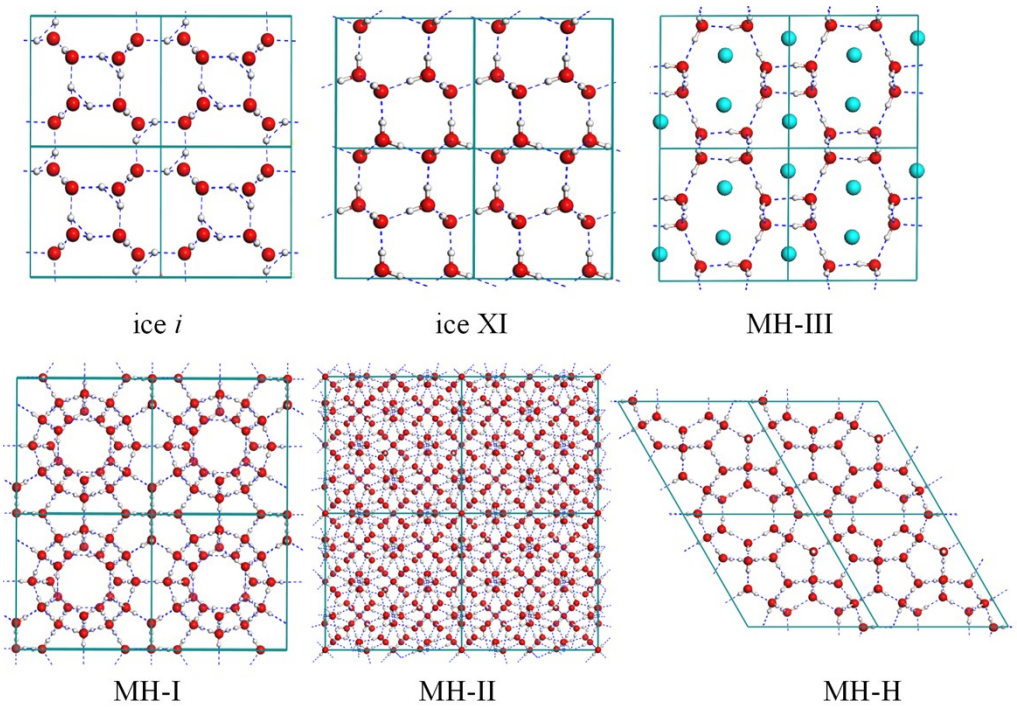

Figure S1.

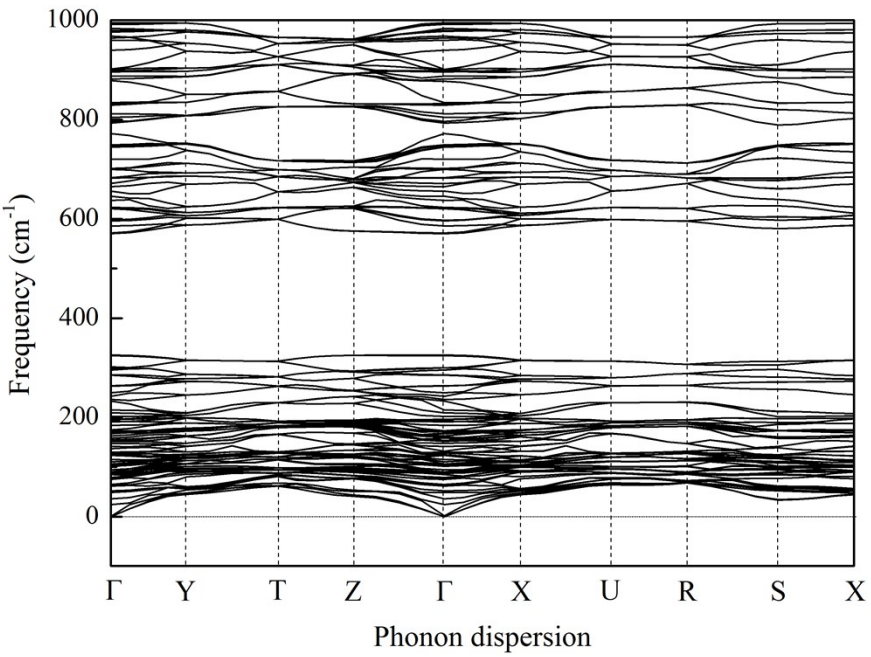

Figure S1. Phonon dispersion for MH-IV hydrate (at 0 GPa) from vdW-DF2 DFT calculations. Definition of special points in the Brillouin zone: Γ - (0.0, 0.0, 0.0), Y - (0.0, 0.5, 0.0), T - (0.0, 0.5, 0.5), Z - (0.0, 0.0, 0.5), X - (0.5, 0.0, 0.0), U - (0.5, 0.0, 0.5), R - (0.5, 0.5, 0.5), S - (0.5, 0.5, 0.0).

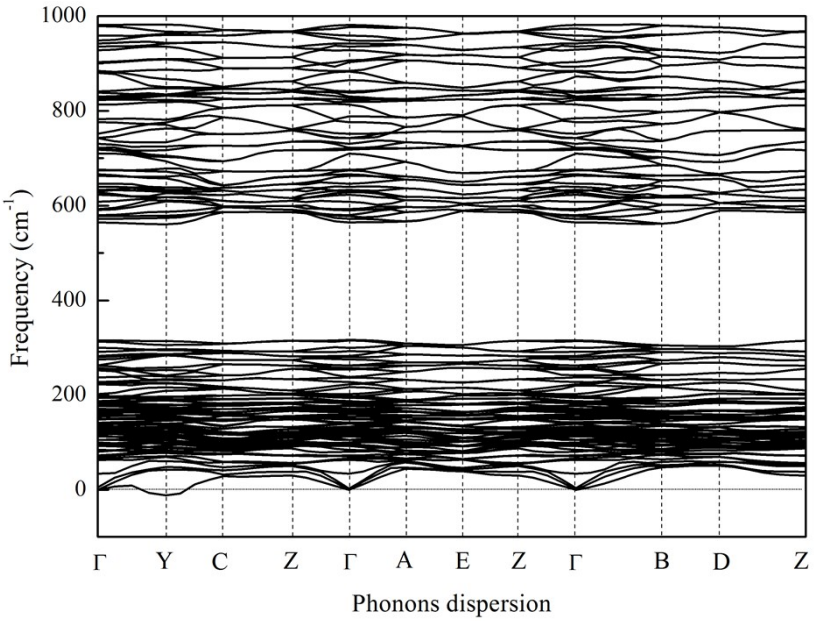

Figure S2. Phonon dispersion for MH-V hydrate (at 0 GPa) from vdW-DF2 DFT calculations. Definition of special points in the Brillouin zone: Γ - (0.0, 0.0, 0.0), Y - (0.5, 0.0, 0.0), C - (0.5, 0.5, 0.0), Z- (0.0, 0.5, 0.0), A- (-0.5, 0.0, 0.5), E - (-0.5, 0.5, 0.5), B - (0.0, 0.0, 0.5), D - (0.0, 0.5, 0.5).

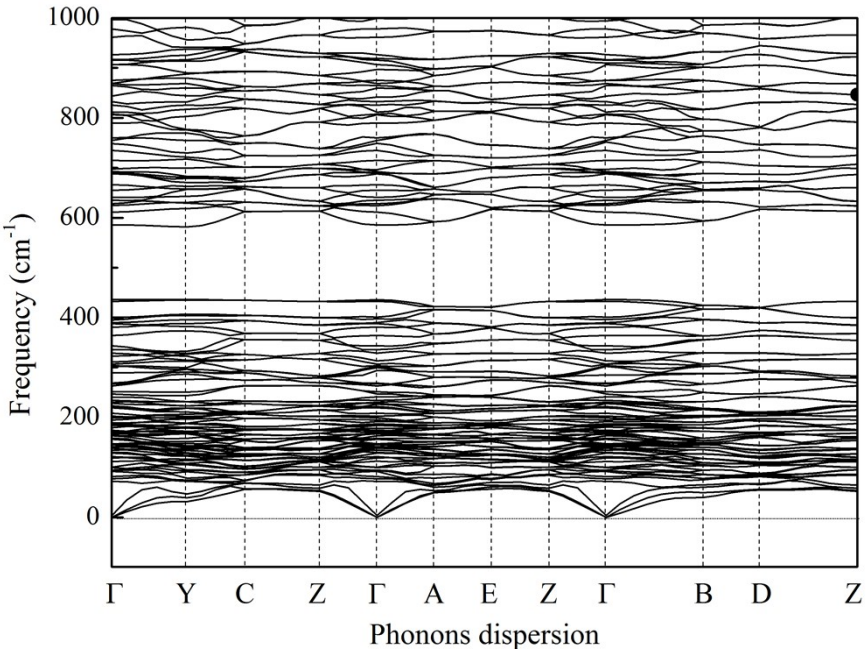

Figure S3. Phonon dispersion for MH-V hydrate (at 4 GPa) from vdW-DF2 DFT calculations. Definition of special points in the Brillouin zone: Γ - (0.0, 0.0, 0.0), Y - (0.5, 0.0, 0.0), C - (0.5, 0.5, 0.0), Z- (0.0, 0.5, 0.0), A- (-0.5, 0.0, 0.5), E - (-0.5, 0.5, 0.5), B - (0.0, 0.0, 0.5), D - (0.0, 0.5, 0.5).

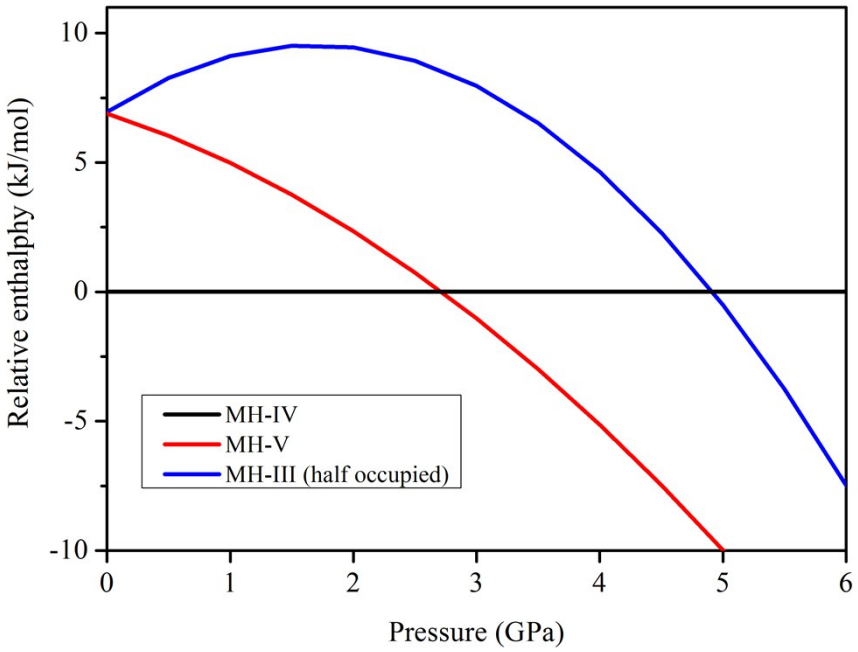

Figure S4. The relative enthalpy *vs*. pressure for crystal hydrates of MH-V and half occupied MH-III by taking MH-IV as a reference. The crossover pressures between MH-IV and MH-V, MH-IV and half occupied MH-III are 2.7 GPa, and 4.9 GPa respectively.