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

Delving into guest-free and He-lled sI and sII clathrate hydrates: a first-principles computational study

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Supplementary material

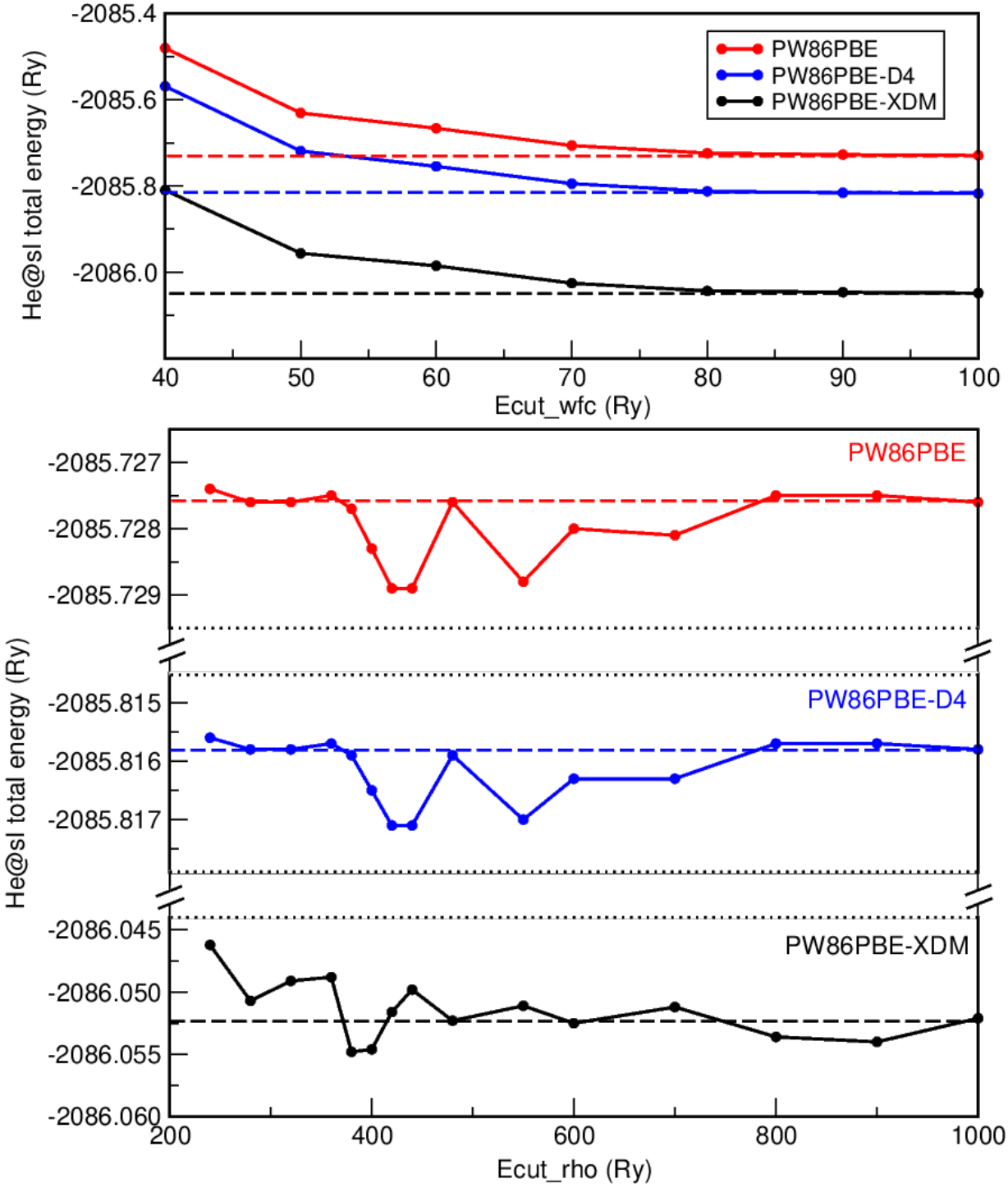

Figure S1: Convergence of He@sI total energies (in Ry) vs the energy cutoff for the plane−wave expansion of the wavefunctions Ecut_wfc and charge density Ecut_rho (in Ry) obtained from single point calculations considering the PW86PBE and PW86PBE−XDM/D4 functionals.

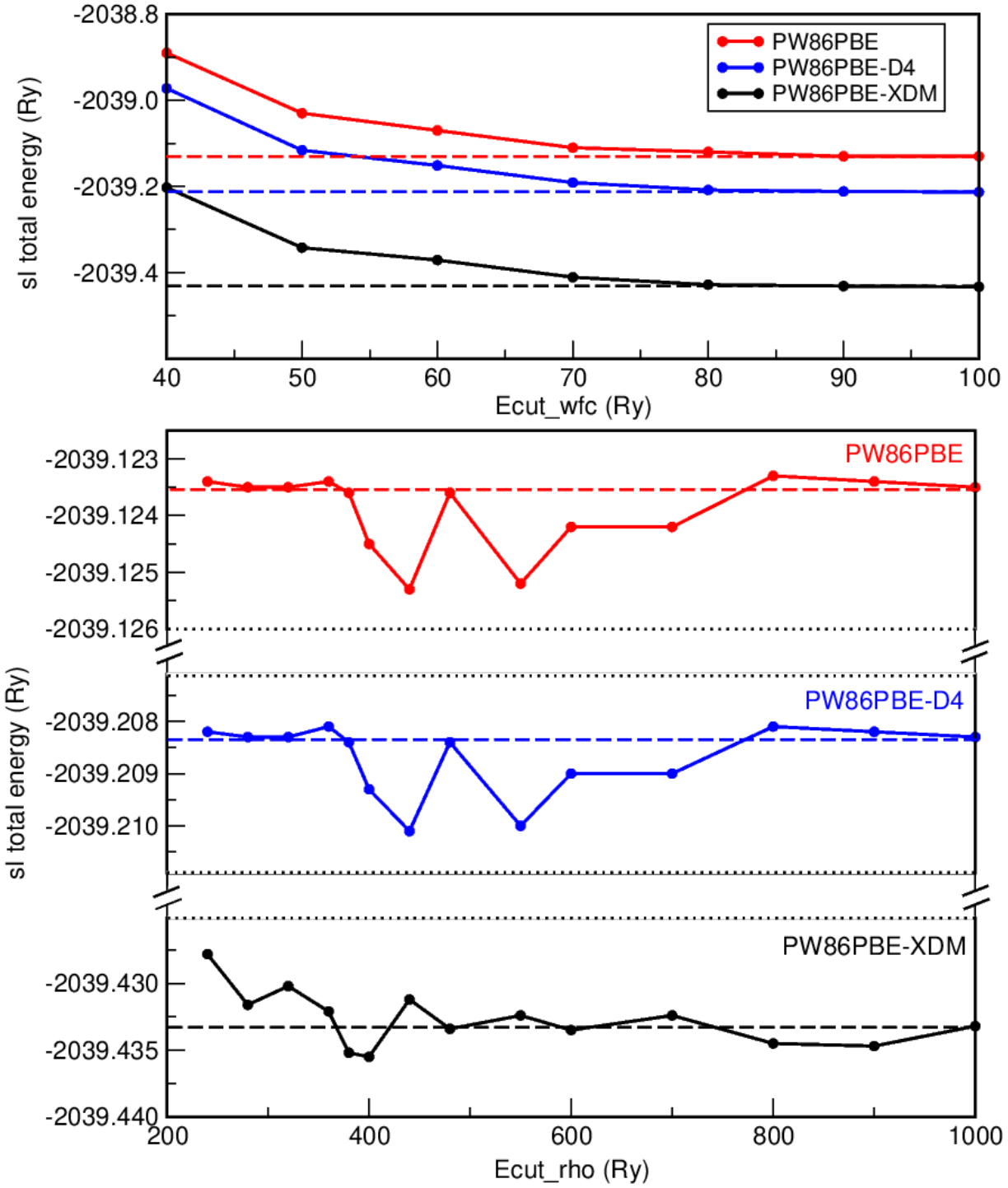

Figure S2: Convergence of sI total energies (in Ry) vs the energy cutoff for the plane−wave expansion of the wavefunctions Ecut_wfc and charge density Ecut_rho (in Ry) obtained from single point calculations considering the PW86PBE and PW86PBE−XDM/D4 functionals.

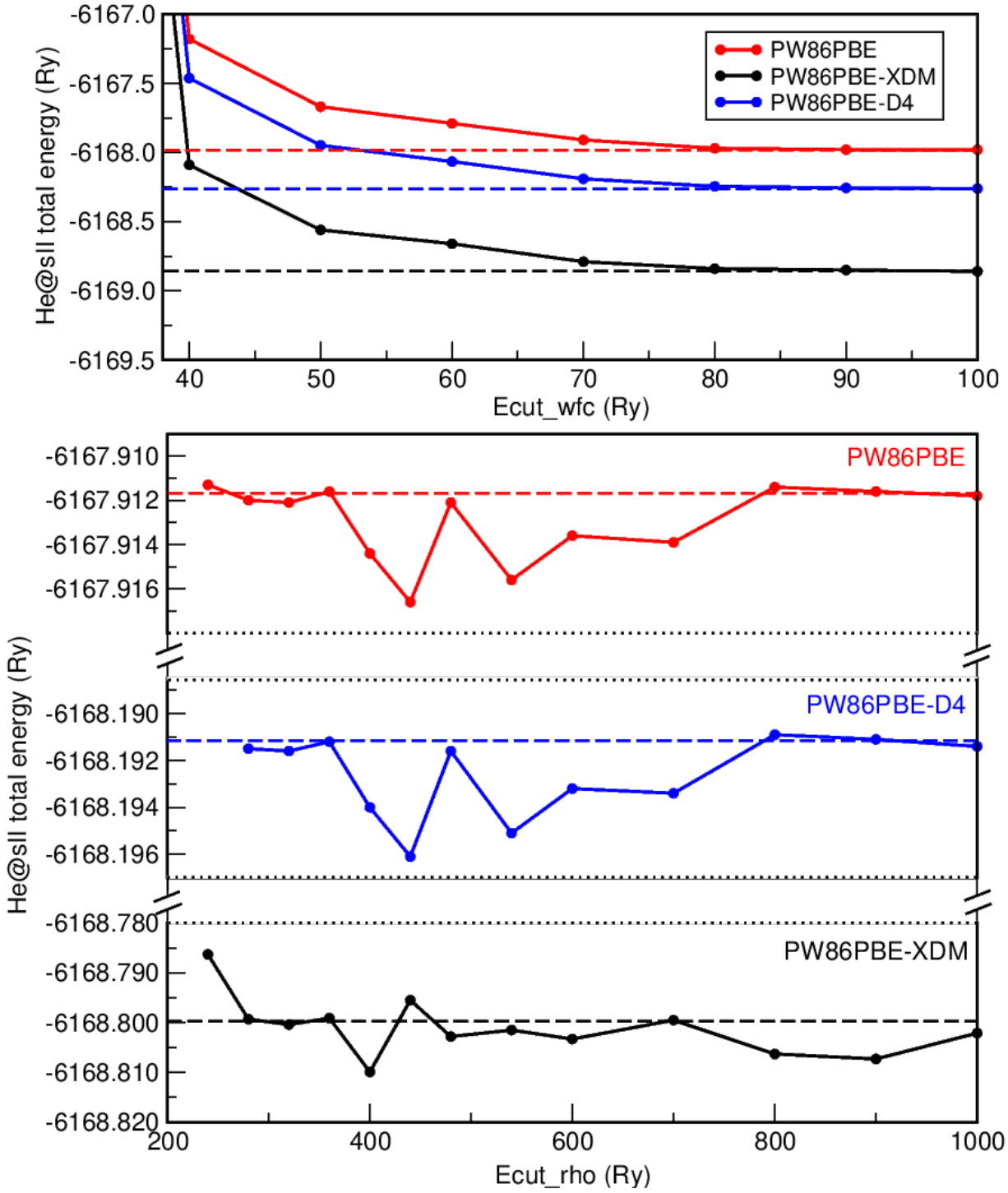

Figure S3: Convergence of He@sII total energies (in Ry) vs the energy cutoff for the plane-wave expansion of the wavefunctions Ecut_wfc and charge density Ecut_rho (in Ry) obtained from single point calculations considering the PW86PBE and PW86PBE−XDM/D4 functionals.

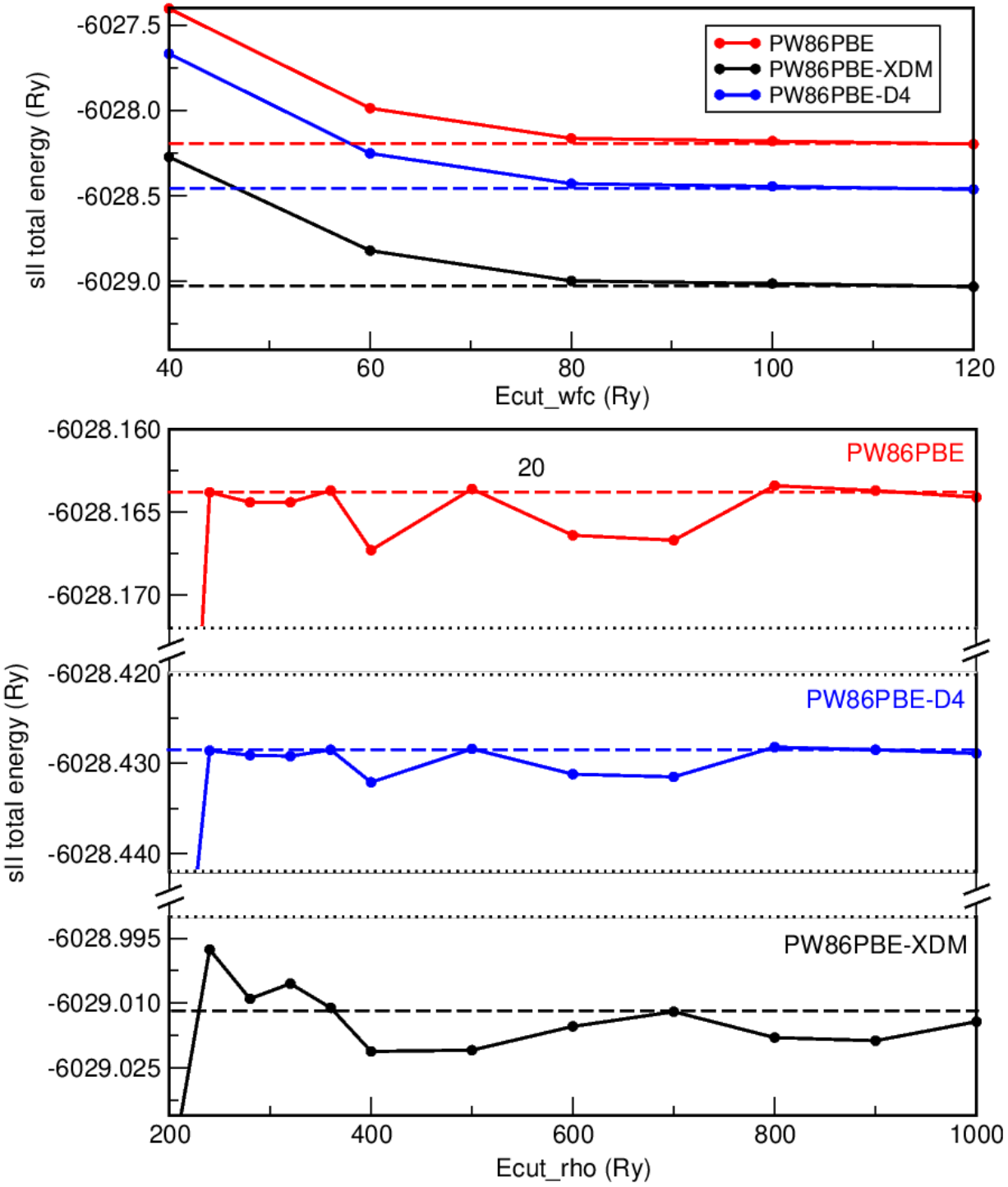

Figure S4: Convergence of sII total energies (in Ry) vs the energy cutoff for the plane-wave expansion of the wavefunctions Ecut_wfc and charge density Ecut_rho (in Ry) obtained from single point calculations considering the PW86PBE and PW86PBE−XDM/D4 functionals.

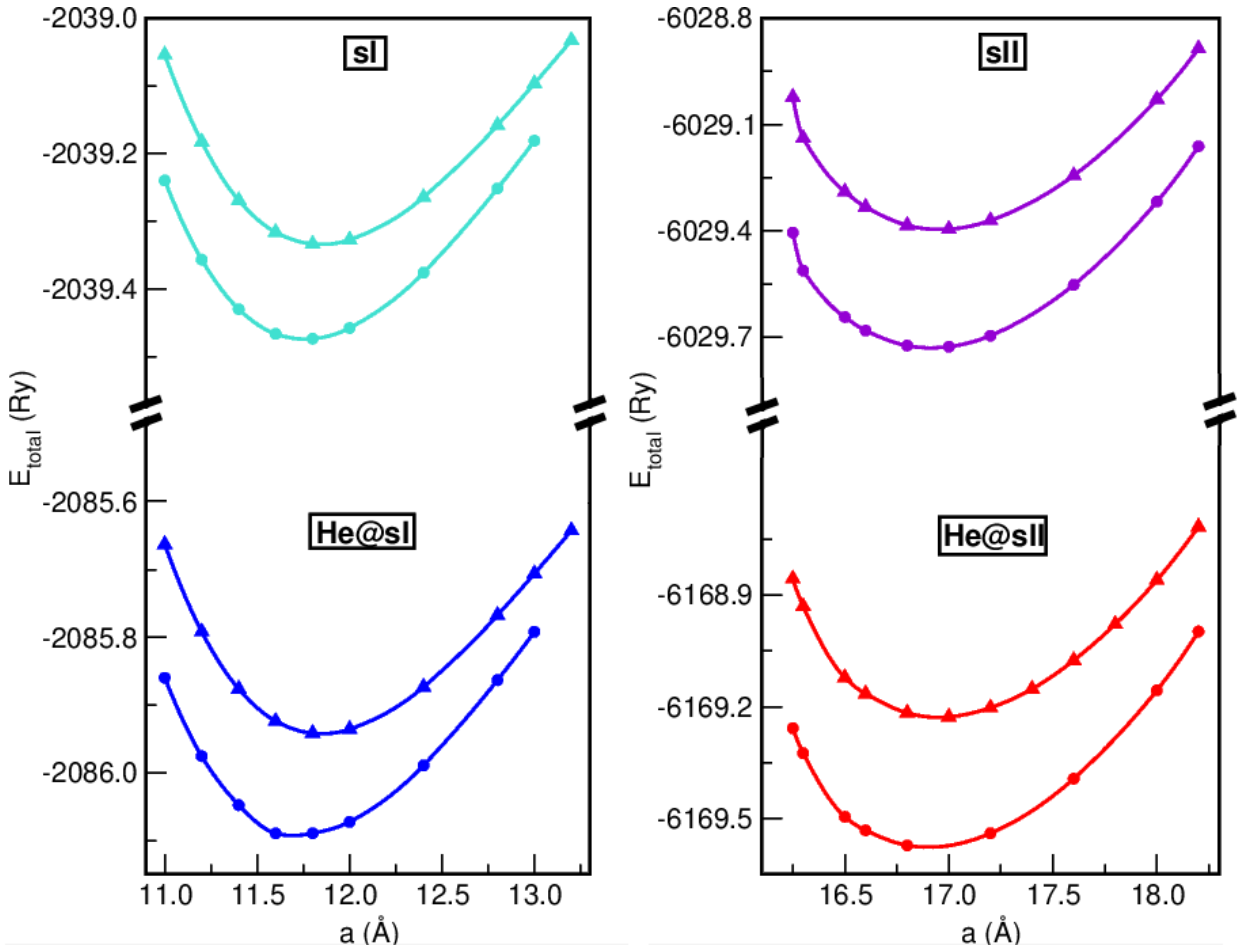

Figure S5: Total energies (in Ry) of the fully occupied He@sI clathrate and the empty sI hydrate (left panel), and of the fully occupied He@sII clathrate and the empty sII hydrate (right panel), as a function of the lattice constant a (in Å). Solid lines correspond to the MEOS fits.

Table S1: Cohesive energies per water molecule (in kcal/mol) (see Fig. 2) corresponding to PW86PBE-XDM computations for the He-filled and empty sI/sII unit cells as a function of the lattice parameter, a.

	He@sI		**sI**		**He@sII**		**sII**
a(Å)	ΔE_{coh}**(kcal/mol)**	a(Å)	ΔE_{coh}**(kcal/mol)**	a(Å)	ΔE_{coh}**(kcal/mol)**	a(Å)	ΔE_{coh}**(kcal/mol)**
11.0	-14.80	11.0	-14.69	16.25	-15.59	16.25	-15.49
11.2	-15.60	11.2	-15.48	16.3	-15.75	16.3	-15.74
11.4	-16.09	11.4	-15.98	16.4	-15.87	16.35	-15.69
11.6	-16.37	11.6	-16.23	16.5	-16.14	16.4	-15.77
11.8	-16.37	11.8	-16.28	16.6	-16.23	16.5	-16.04
12.0	-16.26	12.0	-16.17	16.8	-16.32	16.6	-16.12
12.4	-15.69	12.4	-15.62	17.2	-16.25	16.8	-16.22
12.8	-14.83	12.8	-14.77	17.6	-15.91	17.0	-16.23
13.0	-14.34	13.0	-14.29	18.0	-15.36	17.2	-16.16
				18.2	-15.00	17.6	-15.83
						18.0	-15.29
						18.2	-14.93

Table S2: Cohesive energies per water molecule (in kcal/mol) (see Fig. 2) corresponding to PW86PBE-D4 computations for the He-filled and empty sI/sII unit cells as a function of the lattice parameter, a.

	He@sI		**sI**		**He@sII**		**sII**
a(Å)	ΔE_{coh}**(kcal/mol)**	a(Å)	ΔE_{coh}**(kcal/mol)**	a(Å)	ΔE_{coh}**(kcal/mol)**	a(Å)	ΔE_{coh}**(kcal/mol)**
11.0	-13.59	11.0	-13.55	16.25	-14.79	16.25	-14.73
11.2	-14.46	11.2	-14.42	16.3	-14.96	16.3	-15.00
11.4	-15.04	11.4	-15.01	16.5	-15.41	16.35	-14.97
11.6	-15.37	11.6	-15.33	16.6	-15.51	16.4	-15.06
11.8	-15.49	11.8	-15.45	16.8	-15.62	16.5	-15.35
12.0	-15.45	12.0	-15.41	17.0	-15.65	16.6	-15.45
12.4	-15.02	12.4	-14.98	17.2	-15.59	16.8	-15.57
12.8	-14.30	12.8	-14.26	17.4	-15.48	17.0	-15.59
13.0	-13.88	13.0	-13.84	17.6	-15.30	17.2	-15.54
13.2	-13.45	13.2	-13.40	18.0	-14.80	17.6	-15.24
				18.2	-14.47	18.0	-14.75
						18.2	-14.42