Supplementary Materials: Tetrahydrofuran (THF)-Mediated Structure of THF·$(H_2O)_{n=1–10}$: A Computational Study on the Formation of the THF Hydrate

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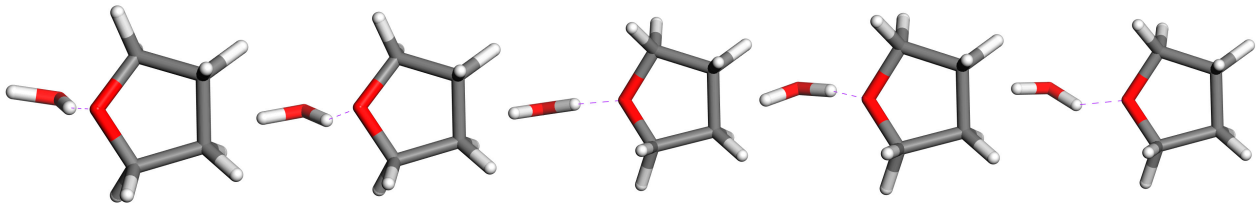
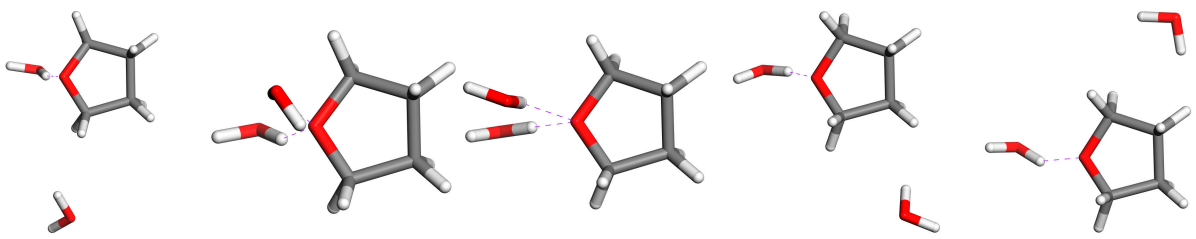
Supplementary Materials:

1. Initial Configurations of Five Uncorrelated THF·$(H_2O)_{n=1–10}$ Clusters



THF·$(H_2O)_1$: (a) (b) (c) (d) (e)



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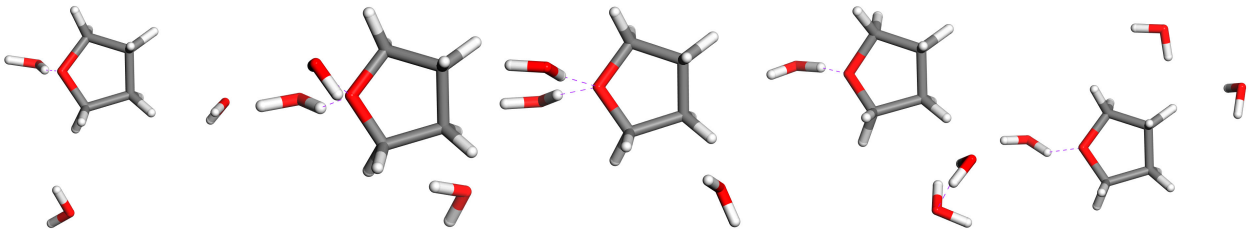
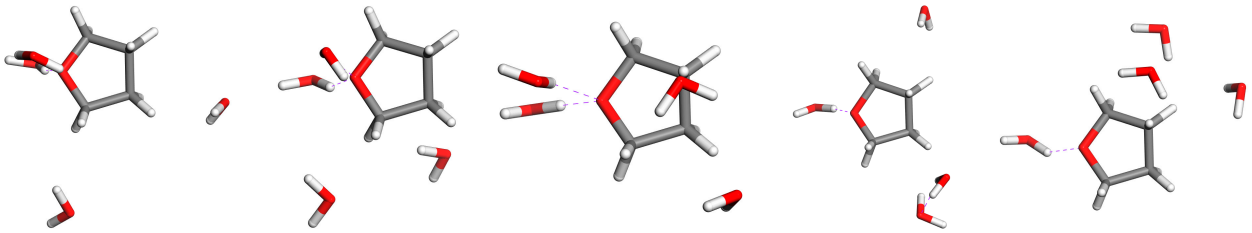


THF·$(H_2O)_3$: (a) (b) (c) (d) (e)



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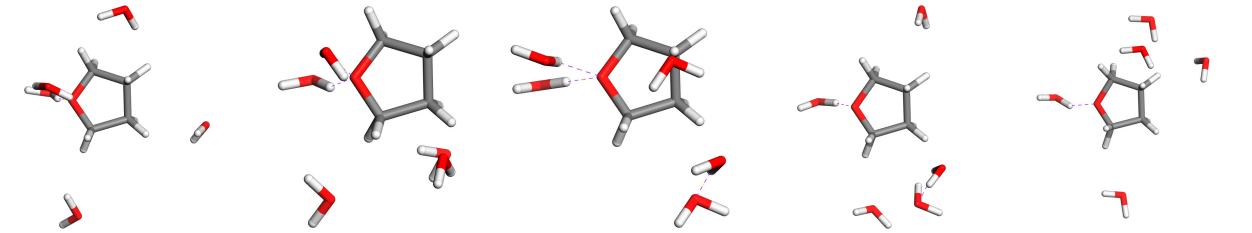
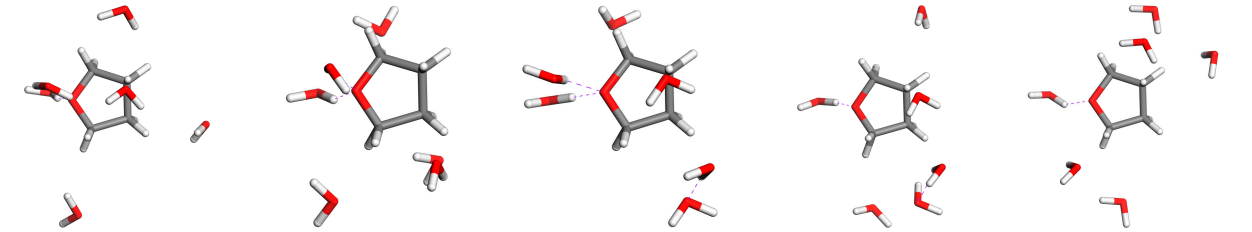


THF·$(H_2O)_5$: (a) (b) (c) (d) (e)



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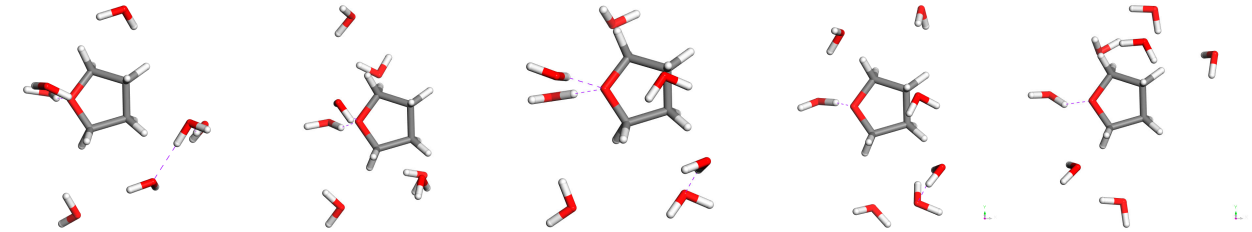

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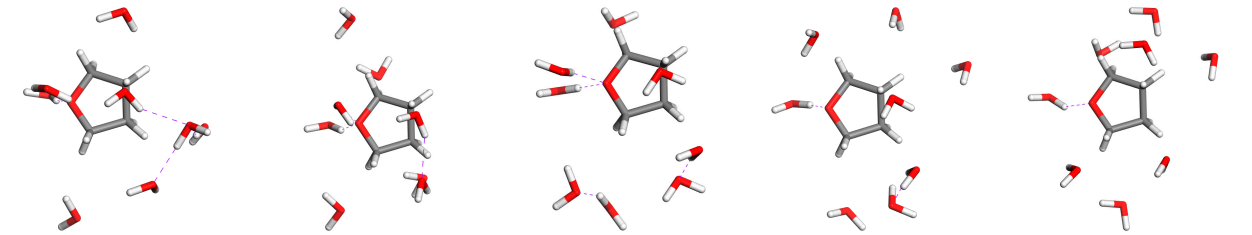

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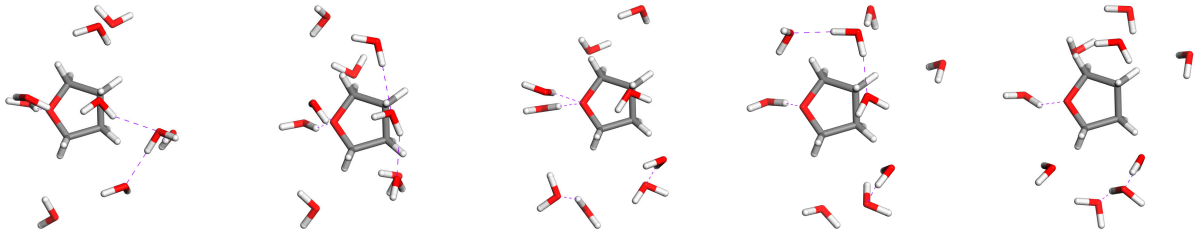
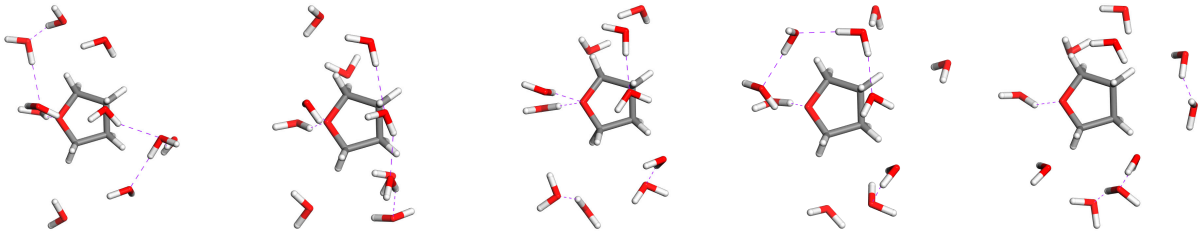


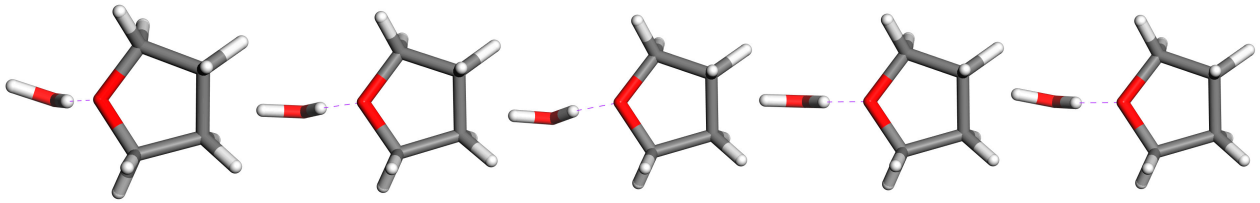
THF·$(H_2O)_9$: (a) (b) (c) (d) (e)



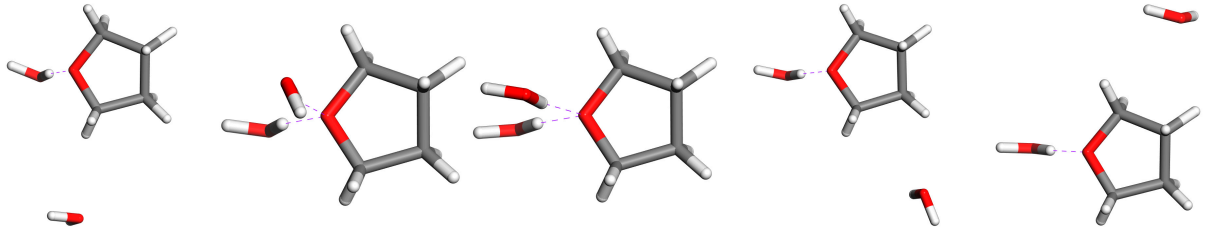
THF·$(H_2O)_{10}$: (a) (b) (c) (d) (e)

Figure S1. Initial configurations of five uncorrelated THF·$(H_2O)_{n=1–10}$ clusters extracted from the ab initio molecular dynamics simulation trajectory.

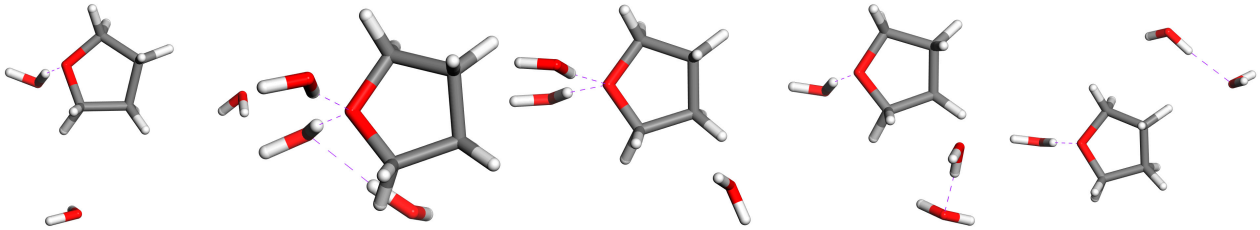
2. Optimized Configurations of Five Uncorrelated THF·$(H_2O)_{n\,=\,1–10}$ Clusters



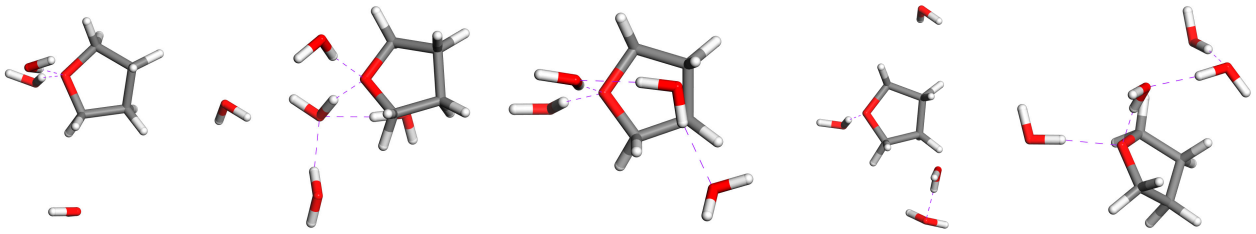
THF·$(H_2O)_1$: (a) (b) (c) (d) (e)



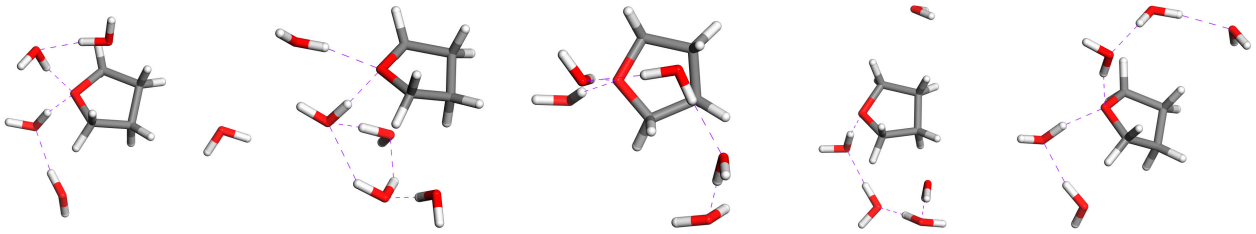
THF·$(H_2O)_2$: (a) (b) (c) (d) (e)



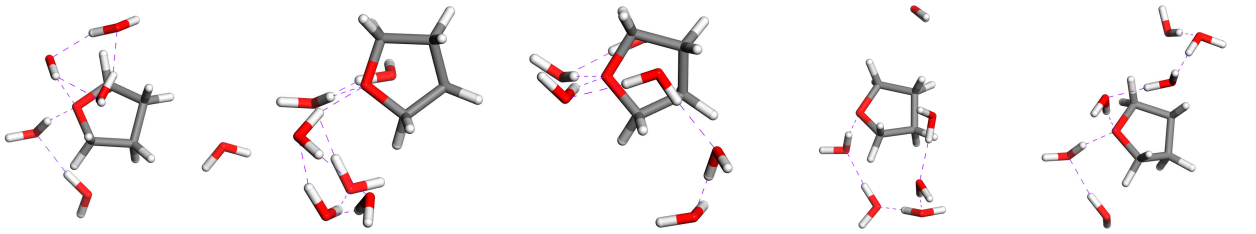
THF·$(H_2O)_3$: (a) (b) (c) (d) (e)



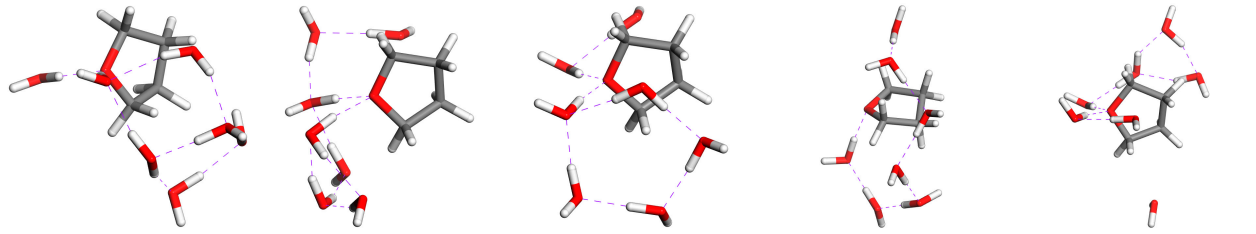
THF·$(H_2O)_4$: (a) (b) (c) (d) (e)



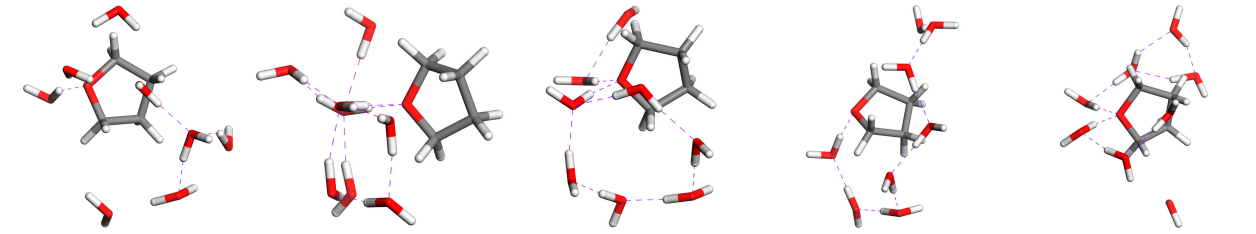
THF·$(H_2O)_5$: (a) (b) (c) (d) (e)



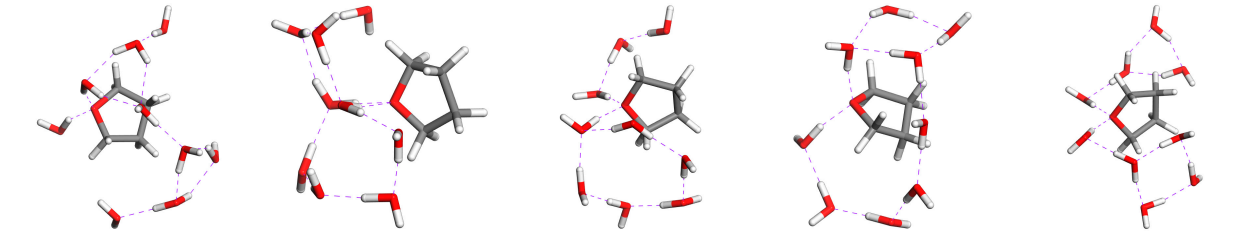
THF·$(H_2O)_6$: (a) (b) (c) (d) (e)



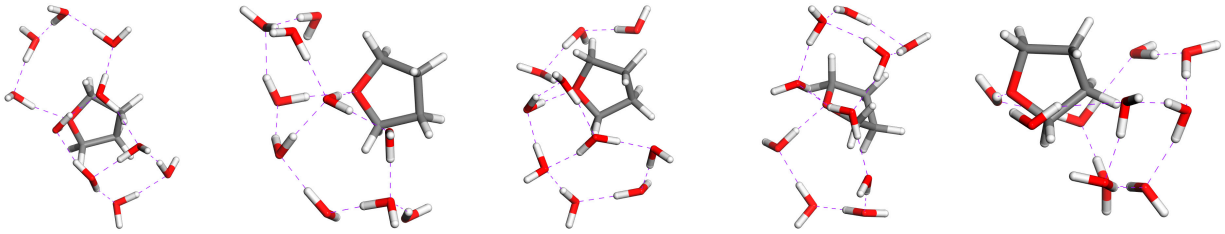
THF·$(H_2O)_7$: (a) (b) (c) (d) (e)



THF·$(H_2O)_8$: (a) (b) (c) (d) (e)



THF·$(H_2O)_9$: (a) (b) (c) (d) (e)



THF·$(H_2O)_{10}$: (a) (b) (c) (d) (e)

Figure S2. Optimized configurations of five uncorrelated THF·$(H_2O)_{n=1-10}$ clusters.

3. The Distance Between Hydrogen Atoms of THF and the Nearest Water Oxygen Atoms for the Lowest-Energy THF·$(H_2O)_{n=1-10}$ Clusters

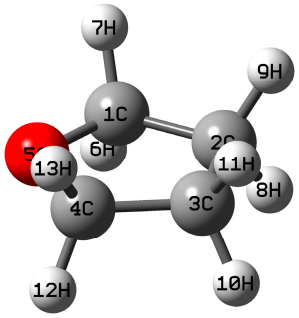
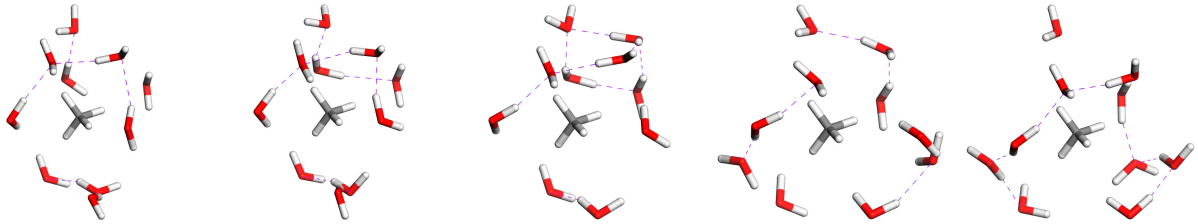


Figure S3. Labels of H atoms of the THF molecule.

Table S1. The distance between H atoms of the THF molecule and their nearest O atoms of water molecules.

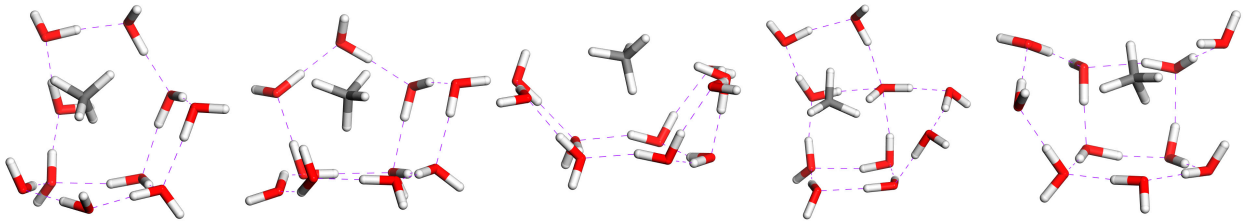
Clusters	Distance (Å)							
	H6	H7	H8	H9	H10	H11	H12	H13
THF·$(H_2O)_1$	**3.162**	4.033	5.356	5.531	4.356	5.563	3.392	4.504
THF·$(H_2O)_2$	3.065	**2.912**	4.839	3.398	4.122	4.896	2.979	3.195
THF·$(H_2O)_3$	2.890	2.963	4.789	3.312	2.675	4.140	**2.653**	2.885
THF·$(H_2O)_4$	3.049	3.010	4.512	2.757	3.622	4.118	2.976	**2.674**
THF·$(H_2O)_5$	**2.808**	3.408	3.952	5.193	2.945	3.185	3.253	3.850
THF·$(H_2O)_6$	2.987	3.992	4.064	5.077	**2.544**	4.316	2.795	2.631
THF·$(H_2O)_7$	**2.619**	2.956	3.096	2.555	2.684	3.497	2.876	2.742
THF·$(H_2O)_8$	2.572	2.748	3.012	3.511	2.623	4.317	3.012	**2.361**
THF·$(H_2O)_9$	2.593	2.783	3.085	3.166	2.736	2.870	2.747	**2.469**
THF·$(H_2O)_{10}$	**2.489**	2.683	2.408	2.463	2.659	3.418	3.719	3.041

4. Initial and Optimized Configurations of Five Uncorrelated CH_4·$(H_2O)_{10}$ Clusters



(a) (b) (c) (d) (e)

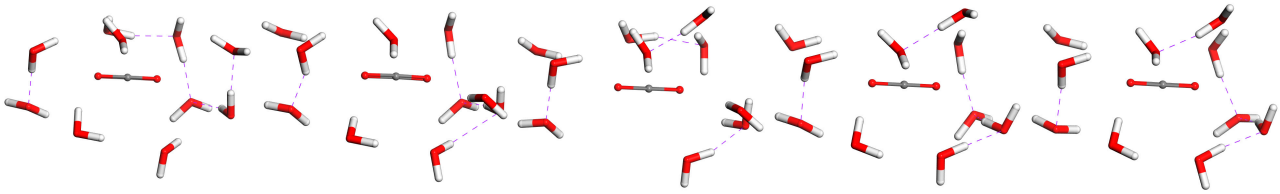
Figure S4. Initial configurations of five uncorrelated CH_4·$(H_2O)_{10}$ clusters, which were obtained by the same procedure as the THF·$(H_2O)_{n=1–10}$ clusters.



(a) 0.383 eV (b) 0.385 eV (c) 0.387 eV (d) 0.374 eV (e) 0.389 eV

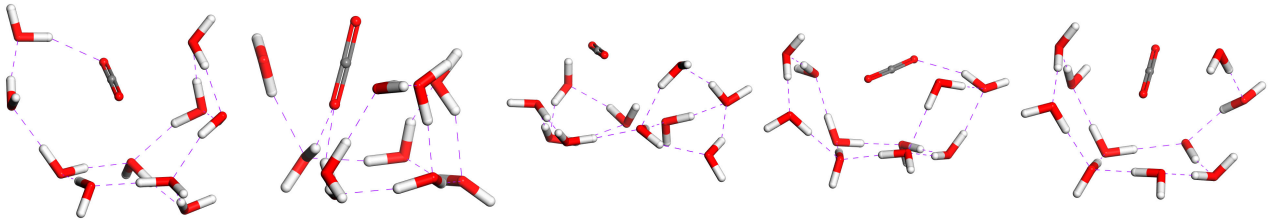
Figure S5. Optimized configurations of five uncorrelated CH_4·$(H_2O)_{10}$ clusters and their stabilization energies, optimized at the PBE-D/TNP level.

5. Initial and Optimized Configurations of Five Uncorrelated CO_2·$(H_2O)_{10}$ Clusters



(a) (b) (c) (d) (e)

Figure S6. Initial configurations of five uncorrelated CO_2·$(H_2O)_{10}$ clusters, which were obtained by the same procedure as the THF·$(H_2O)_{n=1–10}$ clusters.

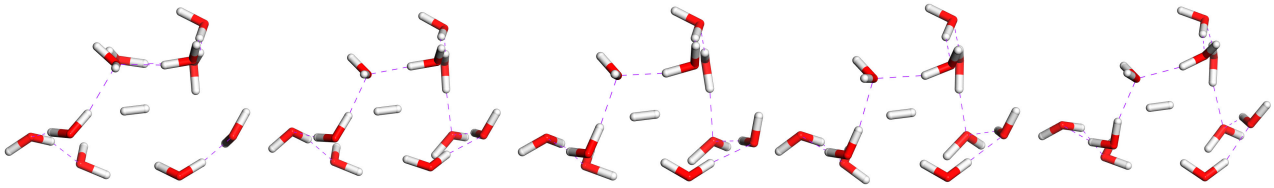


(a) 0.369 eV (b) 0.339 eV (c) 0.350 eV **(d) 0.383 eV** (e) 0.373 eV

Figure S7. Optimized configurations of five uncorrelated CO_2·$(H_2O)_{10}$ clusters and their

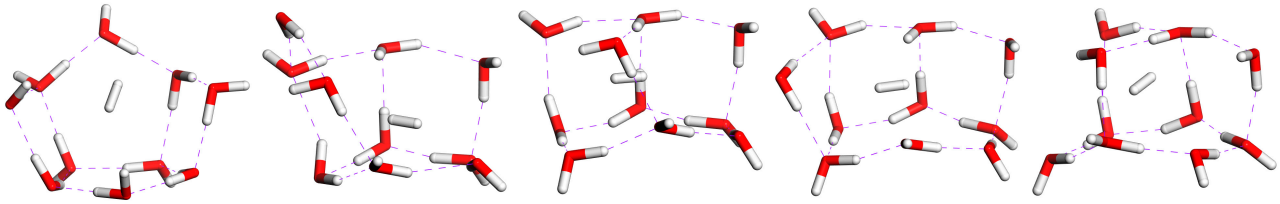
stabilization energies, optimized at the PBE-D/TNP level.

6. Initial and Optimized Configurations of Five Uncorrelated H_2·$(H_2O)_{10}$ Clusters



(a) (b) (c) (d) (e)

Figure S8. Initial configurations of five uncorrelated H_2·$(H_2O)_{10}$ clusters, which were obtained by the same procedure as the THF·$(H_2O)_{n=1–10}$ clusters.



(a) 0.350 eV (b) 0.348 eV (c) 0.345 eV (d) 0.346 eV (e) 0.337 eV

Figure S9. Optimized configurations of five uncorrelated H_2·$(H_2O)_{10}$ clusters and their stabilization energies, optimized at the PBE-D/TNP level.

7. The Stabilization Energies of Clusters Calculated Using Different Functionals and Basis Sets

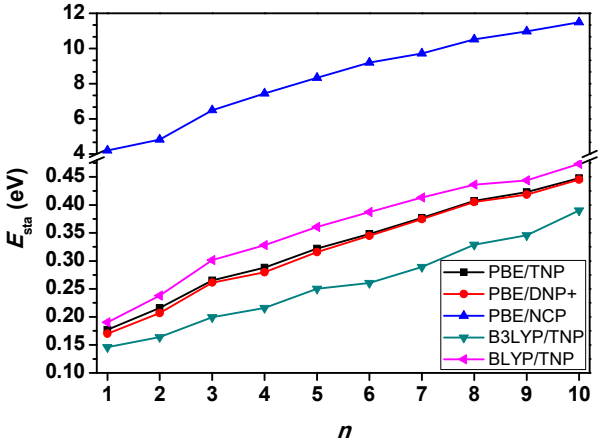


Figure S10. The stabilization energies of the THF·$(H_2O)_{n=1–10}$ clusters shown in Figure 2, calculated at the different levels.

Table S2. The stabilization energy (E_{sta}) of the pentagonal water ring plus a guest (CH_4, CO_2, H_2, and THF), calculated at the different functionals and basis sets.

Guest	PBE/TNP		PBE/DNP+		PBE/NCP		B3LYP/TNP		BLYP/TNP	
	without THF	with THF	without THF	with THF	without THF	with THF	without THF	with THF	without THF	with THF
CH_4	0.325	0.346	0.319	0.340	8.329	8.350	0.253	0.273	0.364	0.387
CO_2	0.326	0.365	0.320	0.360	8.331	8.371	0.255	0.294	0.365	0.403
H_2	0.279	0.340	0.274	0.335	8.281	8.343	0.205	0.267	0.314	0.379
THF	0.382	0.399	0.376	0.393	8.387	8.404	0.309	0.327	0.420	0.438

Table S3. The stabilization energy (E_{sta}) of the hexagonal water ring plus a guest (CH_4, CO_2, H_2, and THF), calculated at the different functionals and basis sets.

Guest	PBE/TNP		PBE/DNP+		PBE/NCP		B3LYP/TNP		BLYP/TNP	
	without THF	with THF	without THF	with THF	without THF	with THF	without THF	with THF	without THF	with THF
CH_4	0.340	0.364	0.336	0.361	9.187	9.212	0.260	0.288	0.375	0.400
CO_2	0.352	0.371	0.350	0.368	9.200	9.228	0.269	0.304	0.390	0.419
H_2	0.294	0.355	0.291	0.352	9.139	9.197	0.227	0.277	0.326	0.388
THF	0.394	0.411	0.390	0.407	9.243	9.259	0.329	0.338	0.433	0.449