Supporting Material for:
Hydrocarbon/Water Interactions:
Encouraging Energetics and Structures from DFT but Disconcerting Discrepancies for Hessian Indices

Kari L. Copeland and Gregory S. Tschumper*

Department of Chemistry and Biochemistry
University of Mississippi, University, Mississippi 38677–1848 USA

*Corresponding Author: tschumpr@olemiss.edu

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TABLE S1. CCSD(T) CBS limit interaction energies (E_{int} in kcal mol^{-1}) for B3LYP stationary points of hydrocarbon/water structures.

Structure	$E_{int}^{MP2/CBS}$[a]	$\delta_{MP2}^{CCSD(T)}$[b]	$E_{int}^{CCSD(T)/CBS}$[c]
CH_4/H_2O			
OH $\cdots$ C	−0.89	−0.03	−0.92
CH $\cdots$ O	−0.60	−0.03	−0.63
C_2H_6/H_2O			
CH $\cdots$ O	*d*	*d*	*d*
OH $\cdots$ C	−0.97	−0.05	−1.02
C_2H_2/H_2O			
CH $\cdots$ O	−2.85	−0.03	−2.88
CH $\cdots$ O(p)	−2.86	−0.03	−2.89
OH $\cdots\pi$	−2.63	+0.11	−2.52
$OH_2\cdots\pi$	−1.89	+0.02	−1.87
C_4H_2/H_2O			
CH $\cdots$ O	−3.36	−0.04	−3.40
CH $\cdots$ O(p)	−3.37	−0.04	−3.40
OH $\cdots\pi$	−2.34	+0.09	−2.25
$OH_2\cdots\pi$	*d*	*d*	*d*
C_2H_4/H_2O			
OH $\cdots\pi$	−2.69	+0.16	−2.52
$CH_2\cdots$ O	−0.74	−0.02	−0.76
$CH_2\cdots$ O(π)	−1.21	−0.01	−1.22
C_4H_6/H_2O			
CH $\cdots$ O	−1.10	−0.03	−1.13
$CH_2\cdots$ O	−1.40	−0.02	−1.42
OH$\cdots\pi$	−2.91	+0.18	−2.73
C_4H_4/H_2O			
CH $\cdots$ O(p)	−1.37	−0.02	−1.39
CH $\cdots$ O	−1.49	−0.02	−1.51
OH $\cdots\pi$	−2.91	+0.25	−2.66
$OH_2\cdots\pi$	−3.23	+0.25	−2.98
C_5H_6/H_2O			
CH $\cdots$ O	−1.23	−0.04	−1.28
OH $\cdots\pi$	−3.65	+0.25	−3.40
$OH_2\cdots\pi$	−3.77	+0.19	−3.58
C_6H_6/H_2O			
CH $\cdots$ O	−1.24	−0.03	−1.27
CH $\cdots$ O(np)	−1.45	−0.02	−1.47
CH $\cdots$ O(p)	−1.26	−0.02	−1.28
OH $\cdots\pi$	−3.05	+0.19	−2.85
$OH_2\cdots\pi$	−3.04	+0.15	−2.89

[a] MP2-R12/K2−−

[b] $\delta_{MP2}^{CCSD(T)} = E_{int}^{CCSD(T)/haTZ} - E_{int}^{MP2/haTZ}$

[c] $E_{int}^{CCSD(T)/CBS} = E_{int}^{MP2/CBS} + \delta_{MP2}^{CCSD(T)}$

[d] Collapses to different stationary point. (See text for details.)

TABLE S2. CCSD(T) CBS limit interaction energies (E_{int} in kcal mol^{-1}) for B97-D stationary points of hydrocarbon/water structures.

Structure	$E_{int}^{MP2/CBS}$[a]	$\delta_{MP2}^{CCSD(T)}$[b]	$E_{int}^{CCSD(T)/CBS}$[c]
CH_4/H_2O			
OH $\cdots$ C	−0.94	−0.04	−0.97
CH $\cdots$ O	−0.62	−0.03	−0.65
C_2H_6/H_2O			
CH $\cdots$ O	−1.30	−0.03	−1.32
OH $\cdots$ C	−1.01	−0.05	−1.07
C_2H_2/H_2O			
CH $\cdots$ O	−2.73	−0.04	−2.77
CH $\cdots$ O(p)	−2.79	−0.02	−2.81
OH $\cdots\pi$	−2.62	+0.11	−2.51
$OH_2\cdots\pi$	−1.96	+0.05	−1.91
C_4H_2/H_2O			
CH $\cdots$ O	−3.21	−0.05	−3.26
CH $\cdots$ O(p)	−3.23	−0.04	−3.27
OH $\cdots\pi$	−2.36	+0.11	−2.24
$OH_2\cdots\pi$	−1.85	+0.06	−1.79
C_2H_4/H_2O			
OH $\cdots\pi$	−2.73	+0.18	−2.55
$CH_2\cdots$ O	−0.78	−0.02	−0.80
$CH_2\cdots$ O(π)	−1.27	−0.01	−1.28
C_4H_6/H_2O			
CH $\cdots$ O	−1.12	−0.02	−1.14
$CH_2\cdots$ O	−1.45	−0.02	−1.47
OH$\cdots\pi$	−3.25	+0.24	−3.01
C_4H_4/H_2O			
CH $\cdots$ O(p)	−1.36	−0.02	−1.38
CH $\cdots$ O	−1.45	−0.04	−1.49
OH $\cdots\pi$	−3.09	+0.31	−2.78
$OH_2\cdots\pi$	−3.63	+0.39	−3.24
C_5H_6/H_2O			
CH $\cdots$ O	−1.20	−0.06	−1.27
OH $\cdots\pi$	*d*	*d*	*d*
$OH_2\cdots\pi$	−4.12	+0.33	−3.79
C_6H_6/H_2O			
CH $\cdots$ O	*d*	*d*	*d*
CH $\cdots$ O(np)	−1.45	−0.02	−1.47
CH $\cdots$ O(p)	−1.26	−0.02	−1.28
OH $\cdots\pi$	−3.58	+0.30	−3.28
$OH_2\cdots\pi$	−3.48	+0.32	−3.17

[a] MP2-R12/K2−−

[b] $\delta_{MP2}^{CCSD(T)} = E_{int}^{CCSD(T)/haTZ} - E_{int}^{MP2/haTZ}$

[c] $E_{int}^{CCSD(T)/CBS} = E_{int}^{MP2/CBS} + \delta_{MP2}^{CCSD(T)}$

[d] Collapses to different stationary point. (See text for details.)

TABLE S3. CCSD(T) CBS limit interaction energies (E_{int} in kcal mol^{-1}) for ωB97X-D stationary points of hydrocarbon/water structures.

Structure	$E_{int}^{MP2/CBS}$[a]	$\delta_{MP2}^{CCSD(T)}$[b]	$E_{int}^{CCSD(T)/CBS}$[c]
CH_4/H_2O			
OH $\cdots$ C	−0.94	−0.04	−0.98
CH $\cdots$ O	−0.62	−0.03	−0.65
C_2H_6/H_2O			
CH $\cdots$ O	−1.29	−0.03	−1.32
OH $\cdots$ C	−1.03	−0.06	−1.09
C_2H_2/H_2O			
CH $\cdots$ O	−2.80	−0.05	−2.85
CH $\cdots$ O(p)	−2.86	−0.03	−2.89
OH $\cdots\pi$	−2.65	+0.12	−2.53
$OH_2\cdots\pi$	−1.97	+0.03	−1.94
C_4H_2/H_2O			
CH $\cdots$ O	−3.31	−0.05	−3.36
CH $\cdots$ O(p)	−3.36	−0.04	−3.40
OH $\cdots\pi$	−2.37	+0.11	−2.26
$OH_2\cdots\pi$	−1.86	−0.01	−1.87
C_2H_4/H_2O			
OH $\cdots\pi$	−2.74	+0.18	−2.56
$CH_2\cdots$ O	−0.81	−0.03	−0.84
$CH_2\cdots$ O(π)	−1.30	−0.02	−1.32
C_4H_6/H_2O			
CH $\cdots$ O	−1.13	−0.03	−1.16
$CH_2\cdots$ O	−1.49	−0.03	−1.52
OH$\cdots\pi$	−3.22	+0.19	−3.03
C_4H_4/H_2O			
CH $\cdots$ O(p)	−1.38	−0.03	−1.41
CH $\cdots$ O	−1.44	−0.05	−1.50
OH $\cdots\pi$	−3.09	+0.31	−2.78
$OH_2\cdots\pi$	−3.60	+0.31	−3.30
C_5H_6/H_2O			
CH $\cdots$ O	−1.18	−0.08	−1.25
OH $\cdots\pi$	*d*	*d*	*d*
$OH_2\cdots\pi$	−4.09	+0.26	−3.82
C_6H_6/H_2O			
CH $\cdots$ O	*d*	*d*	*d*
CH $\cdots$ O(np)	−1.50	−0.02	−1.52
CH $\cdots$ O(p)	−1.30	−0.03	−1.32
OH $\cdots\pi$	−3.51	+0.26	−3.25
$OH_2\cdots\pi$	−3.47	+0.26	−3.22

[a] MP2-R12/K2−−

[b] $\delta_{MP2}^{CCSD(T)} = E_{int}^{CCSD(T)/haTZ} - E_{int}^{MP2/haTZ}$

[c] $E_{int}^{CCSD(T)/CBS} = E_{int}^{MP2/CBS} + \delta_{MP2}^{CCSD(T)}$

[d] Collapses to different stationary point. (See text for details.)

TABLE S4. CCSD(T) CBS limit interaction energies (E_{int} in kcal mol^{-1}) for M06-2X stationary points of hydrocarbon/water structures.

Structure	$E_{int}^{MP2/CBS}$[a]	$\delta_{MP2}^{CCSD(T)}$[b]	$E_{int}^{CCSD(T)/CBS}$[c]
CH_4/H_2O			
OH $\cdots$ C	−0.92	−0.04	−0.95
CH $\cdots$ O	−0.61	−0.03	−0.65
C_2H_6/H_2O			
CH $\cdots$ O	−1.26	−0.03	−1.29
OH $\cdots$ C	−1.01	−0.06	−1.20
C_2H_2/H_2O			
CH $\cdots$ O	−2.86	−0.03	−2.89
CH $\cdots$ O(p)	−2.87	−0.02	−2.89
OH $\cdots\pi$	−2.65	+0.14	−2.52
$OH_2\cdots\pi$	−1.93	+0.05	−1.88
C_4H_2/H_2O			
CH $\cdots$ O	−3.37	−0.03	−3.40
CH $\cdots$ O(p)	−3.37	−0.04	−3.40
OH $\cdots\pi$	*d*	*d*	*d*
$OH_2\cdots\pi$	*d*	*d*	*d*
C_2H_4/H_2O			
OH $\cdots\pi$	−2.68	+0.17	−2.51
$CH_2\cdots$ O	−0.83	−0.03	−0.86
$CH_2\cdots$ O(π)	−1.29	−0.03	−1.32
C_4H_6/H_2O			
CH $\cdots$ O	−1.13	−0.03	−1.16
$CH_2\cdots$ O	−1.49	−0.03	−1.52
OH$\cdots\pi$	−3.16	+0.20	−2.96
C_4H_4/H_2O			
CH $\cdots$ O(p)	−1.39	−0.03	−1.41
CH $\cdots$ O	−1.50	−0.03	−1.53
OH $\cdots\pi$	*d*	*d*	*d*
$OH_2\cdots\pi$	−3.60	+0.35	−3.25
C_5H_6/H_2O			
CH $\cdots$ O	−1.26	−0.05	−1.31
OH $\cdots\pi$	*d*	*d*	*d*
$OH_2\cdots\pi$	−4.06	+0.30	−3.76
C_6H_6/H_2O			
CH $\cdots$ O	−1.29	−0.03	−1.32
CH $\cdots$ O(np)	−1.50	−0.02	−1.52
CH $\cdots$ O(p)	−1.30	−0.03	−1.32
OH $\cdots\pi$	−3.47	+0.31	−3.17
$OH_2\cdots\pi$	−3.45	+0.30	−3.15

[a] MP2-R12/K2−−

[b] $\delta_{MP2}^{CCSD(T)} = E_{int}^{CCSD(T)/haTZ} - E_{int}^{MP2/haTZ}$

[c] $E_{int}^{CCSD(T)/CBS} = E_{int}^{MP2/CBS} + \delta_{MP2}^{CCSD(T)}$

[d] Collapses to different stationary point. (See text for details.)

TABLE S5. Interaction energies (E_{int} in kcal mol^{-1}) for the MP2/haTZ optimized structures, and deviations (ΔE_{int} in kcal mol^{-1}) of DFT/haTZ optimized structure from MP2 reference energies.

	MP2	B3LYP	B97-D	ωB97X-D	M06-2X
Structure	E_{int}	ΔE_{int}	ΔE_{int}	ΔE_{int}	ΔE_{int}
CH_4/H_2O					
OH ··· C	−0.99	+0.68	−0.35	−0.04	−0.08
CH ··· O	−0.66	+0.42	+0.11	+0.17	+0.17
C_2H_6/H_2O					
CH ··· O	−1.36	*a*	−0.35	+0.04	−0.13
OH ··· C	−1.17	+0.81	−0.33	+0.02	−0.00
C_2H_2/H_2O					
CH ··· O	−2.97	+0.57	+0.43	+0.20	+0.13
CH ··· O(p)	−2.96	+0.57	+0.49	+0.25	+0.13
OH ···π	−2.82	+0.91	−0.02	+0.11	+0.02
OH_2 ···π	−2.03	+0.87	−0.13	−0.21	−0.34
C_4H_2/H_2O					
CH ··· O	−3.51	+0.67	+0.61	+0.28	+0.17
CH ··· O(p)	−3.51	+0.67	+0.65	+0.32	+0.17
OH ···π	−2.58	+1.12	+0.07	+0.24	*a*
OH_2 ···π	−1.97	*a*	−0.02	−0.11	*a*
C_2H_4/H_2O					
OH ···π	−2.86	+1.05	−0.13	+0.07	+0.03
CH_2 ··· O	−0.93	+0.63	+0.25	+0.28	+0.16
CH_2 ··· O(π)	−1.41	+0.88	+0.35	+0.34	+0.12
C_4H_6/H_2O					
CH ··· O	−1.21	+0.60	+0.24	+0.27	+0.27
CH_2 ··· O	−1.66	+1.01	+0.43	+0.40	+0.21
OH ···π	−3.44	+1.65	−0.05	−0.06	−0.20
C_4H_4/H_2O					
CH ··· O(p)	−1.50	+0.65	+0.31	+0.31	+0.30
CH ··· O	−1.65	+0.67	+0.31	+0.26	+0.31
OH ···π	−3.46	+1.60	+0.08	+0.34	*a*
OH_2 ···π	−3.93	+1.76	−0.24	+0.05	−0.22
C_5H_6/H_2O					
CH ··· O	−1.42	+0.72	+0.33	+0.30	+0.39
OH ···π	−4.46	+2.30	*a*	*a*	*a*
OH_2 ···π	−4.36	+2.50	−0.11	−0.12	−0.48
C_6H_6/H_2O					
CH ··· O	−1.39	+0.73	*a*	*a*	+0.38
CH ··· O(np)	−1.62	+0.78	+0.37	+0.38	+0.41
CH ··· O(p)	−1.40	+0.73	+0.31	+0.34	+0.39
OH ···π	−3.85	+2.31	+0.31	+0.14	−0.08
OH_2 ···π	−3.71	+2.46	+0.23	−0.01	−0.20
Maximum Absolute Error		2.50	0.65	0.40	0.48
Minimum Absolute Error		0.42	0.02	0.01	0.00
Average Absolute Error		1.08	0.27	0.20	0.21

[a] Collapses to different stationary point. (See text for details.)

TABLE S6. The center-of-mass distance (R_{com} in Å) for the MP2 optimized structures, and the deviations (ΔR_{com} in Å) of the DFT optimized strutures from the MP2 reference geometries.

Structure	MP2	B3LYP	B97-D	ωB97X-D	M06-2X
CH_4/H_2O	R_{com}	ΔR_{com}	ΔR_{com}	ΔR_{com}	ΔR_{com}
OH $\cdots$ C	3.31	0.18	0.01	0.03	0.10
CH $\cdots$ O	4.12	0.16	0.11	0.07	0.09
C_2H_6/H_2O					
CH $\cdots$ O	3.40	*a*	0.02	0.05	0.11
OH $\cdots$ C	4.05	0.20	0.00	0.02	0.09
C_2H_2/H_2O					
CH $\cdots$ O	4.25	0.01	0.06	0.10	0.03
CH $\cdots$ O(p)	4.26	0.02	0.17	0.03	0.02
OH $\cdots\pi$	3.10	0.10	0.10	0.02	0.02
$OH_2\cdots\pi$	2.99	0.17	0.07	0.01	0.11
C_4H_2/H_2O					
CH $\cdots$ O	5.52	0.00	0.06	0.09	0.03
CH $\cdots$ O(p)	5.52	0.01	0.16	0.03	0.03
OH $\cdots\pi$	3.54	0.33	0.05	0.11	*a*
$OH_2\cdots\pi$	3.46	*a*	0.01	0.44	*a*
C_2H_4/H_2O					
OH $\cdots\pi$	3.15	0.11	0.08	0.02	0.01
$CH_2\cdots$ O	4.44	0.28	0.21	0.10	0.01
$CH_2\cdots$ O(π)	3.77	0.22	0.16	0.06	0.09
C_4H_6/H_2O					
CH $\cdots$ O	5.48	0.18	0.09	0.04	0.02
$CH_2\cdots$ O	4.47	0.23	0.09	0.06	0.06
OH $\cdots\pi$	2.91	0.64	0.09	0.03	0.10
C_4H_4/H_2O					
CH $\cdots$ O(p)	4.92	0.09	0.13	0.02	0.01
CH $\cdots$ O	4.89	0.08	0.04	0.12	0.00
OH $\cdots\pi$	3.17	0.35	0.20	0.15	*a*
$OH_2\cdots\pi$	2.89	0.57	0.14	0.05	0.13
C_5H_6/H_2O					
CH $\cdots$ O	5.10	0.14	0.05	0.08	0.03
OH $\cdots\pi$	2.89	0.47	*a*	*a*	*a*
$OH_2\cdots\pi$	2.79	0.25	0.02	0.04	0.03
C_6H_6/H_2O					
CH $\cdots$ O	5.33	0.14	*a*	*a*	0.02
CH $\cdots$ O(np)	5.29	0.13	0.15	0.03	0.03
CH $\cdots$ O(p)	5.33	0.14	0.14	0.05	0.03
OH $\cdots\pi$	2.99	0.56	0.05	0.05	0.14
$OH_2\cdots\pi$	2.87	0.35	0.03	0.03	0.05
Max. Absolute Deviation		0.64	0.21	0.44	0.14
Min. Absolute Deviation		0.00	0.00	0.01	0.00
Avg. Absolute Deviation		0.22	0.09	0.07	0.05

[a] Collapses to different stationary point. (See text for details.)

TABLE S7. CBS limit interaction energies (E_{int} in kcal mol^{-1}) and higher-order correlation effects ($\delta_{MP2}^{CCSD(T)}$ in kcal mol^{-1}) for MP2/haTZ optimized alternative benzene/water structures.

Structure	n_i	E_{int}^{MP2}	$E_{int}^{MP2/CBS}$[a]	$\delta_{MP2}^{CCSD(T)}$[b]	$E_{int}^{CCSD(T)/CBS}$[c]	$E_{int}^{CCSD(T)/CBS}$[d]	$E_{int}^{CCSD(T)/CBS}$[d,e]
C_6H_6/H_2O							
$OH\cdots\pi$	1	−3.84	−3.56	+0.32	−3.24	−3.27	−3.14
$OH_2\cdots\pi$	2	−3.70	−3.45	+0.28	−3.17	−3.18	−3.06

[a] MP2-R12/K2−−

[b] $\delta_{MP2}^{CCSD(T)} = E_{int}^{CCSD(T)/haTZ} - E_{int}^{MP2/haTZ}$

[c] $E_{int}^{CCSD(T)/CBS} = E_{int}^{MP2/CBS} + \delta_{MP2}^{CCSD(T)}$

[d] CCSD(T)-F12/VTZ-F12

[e] Counterpoise Corrected

(a) $OH\cdots\pi$ (C_s) (b) $OH_2\cdots\pi$ (C_{2v})

FIG. 1. Alternative configurations of water interacting with benzene

TABLE S8. Cartesian coordinates (in Å) of the CH_4/H_2O OH $\cdots$ C structure.

C	-0.099613	-0.172536	-0.042121
H	-0.070093	-0.121406	1.043218
H	0.911729	-0.199674	-0.438976
H	-0.628788	0.689743	-0.438976
H	-0.621776	-1.076948	-0.338923
H	1.143343	1.980328	0.468439
H	1.753826	3.037717	1.370287
O	1.624280	2.813335	0.444553

MP2/haTZ optimized structure

TABLE S9. Cartesian coordinates (in Å) of the CH_4/H_2O CH $\cdots$ O structure.

C	0.000486	1.921157	0.000000
H	0.512355	2.286726	0.885838
H	0.512355	2.286726	-0.885838
H	-1.022602	2.286603	0.000000
H	0.000542	0.835022	0.000000
O	0.000486	-1.804034	0.000000
H	-0.004727	-2.394873	-0.758631
H	-0.004727	-2.394873	0.758631

MP2/haTZ optimized structure

TABLE S10. Cartesian coordinates (in Å) of the C_2H_6/H_2O CH $\cdots$ O structure.

C	-1.075247	1.022970	0.000000
C	-1.242679	-0.492542	0.000000
H	-1.539643	1.466074	0.879413
H	-0.789388	-0.940914	0.884959
H	-0.023928	1.305432	0.000000
H	-0.789388	-0.940914	-0.884959
H	-1.539643	1.466074	-0.879413
H	-2.293566	-0.777808	0.000000
O	2.153213	-0.364226	0.000000
H	1.303568	-0.816175	0.000000
H	2.800565	-1.075224	0.000000

MP2/haTZ optimized structure

TABLE S11. Cartesian coordinates (in Å) of the C_2H_6/H_2O OH $\cdots$ C structure.

C	0.034033	0.000000	0.156377
C	-0.047652	0.000000	1.678818
H	-0.962757	0.000000	-0.285302
H	-0.575246	0.879569	2.043678
H	0.563165	0.881924	-0.204497
H	0.945796	0.000000	2.123807
H	0.563165	-0.881924	-0.204497
H	-0.575246	-0.879569	2.043678
H	0.332761	0.000000	-2.345476
H	-0.213180	0.000000	-3.761583
O	0.611016	0.000000	-3.266781

MP2/haTZ optimized structure

TABLE S12. Cartesian coordinates (in Å) of the C_2H_2/H_2O CH $\cdots$ O structure.

C	-2.012330	-1.044502	0.00000
H	-2.949542	-1.544494	0.00000
C	-0.941953	-0.472276	0.00000
H	-0.000013	0.029827	0.00000
O	1.951763	1.039920	0.00000
H	2.530531	1.148090	0.76032
H	2.530531	1.148090	-0.76032

MP2/haTZ optimized structure

TABLE S13. Cartesian coordinates (in Å) of the C_2H_2/H_2O CH $\cdots$ O(p) structure.

C	0.000000	0.000000	-2.267802
H	0.000000	0.000000	-3.330038
C	0.000000	0.000000	-1.054077
H	0.000000	0.000000	0.013248
O	0.000000	0.000000	2.207072
H	0.000000	0.760492	2.795549
H	0.000000	-0.760492	2.795549

MP2/haTZ optimized structure

TABLE S14. Cartesian coordinates (in Å) of the C_2H_2/H_2O OH $\cdots \pi$ structure.

C	0.606646	-0.019792	0.988371
C	-0.606646	-0.019792	0.988371
H	1.669929	-0.020118	0.993733
H	-1.669929	-0.020118	0.993733
H	0.000000	-2.143729	-0.018654
O	0.000000	-3.031003	-0.397952
H	0.000000	-2.880098	-1.347227

MP2/haTZ optimized structure

TABLE S15. Cartesian coordinates (in Å) of the C_2H_2/H_2O $OH_2 \cdots \pi$ structure.

O	0.000000	0.000000	-0.203511
C	0.606569	0.000000	3.187160
C	-0.606569	0.000000	3.187160
H	1.669746	0.000000	3.190215
H	-1.669746	0.000000	3.190215
H	0.000000	-0.750779	0.398087
H	0.000000	0.750779	0.398087

MP2/haTZ optimized structure

TABLE S16. Cartesian coordinates (in Å) of the C_4H_2/H_2O CH $\cdots$ O structure.

C	-0.124739	0.000000	0.220631
C	0.006542	0.000000	1.583332
C	-0.241763	0.000000	-0.995276
H	-0.344561	0.000000	-2.059025
C	0.123575	0.000000	2.798362
H	0.225532	0.000000	3.856122
O	-0.553521	0.000000	-4.200373
H	-0.647971	-0.760768	-4.780996
H	-0.647971	0.760768	-4.780996

MP2/haTZ optimized structure

TABLE S17. Cartesian coordinates (in Å) of the C_4H_2/H_2O CH $\cdots$ O(p) structure.

C	0.000000	0.000000	-0.772476
C	0.000000	0.000000	-2.141483
C	0.000000	0.000000	0.449049
H	0.000000	0.000000	1.517746
C	0.000000	0.000000	-3.362136
H	0.000000	0.000000	-4.424798
O	0.000000	0.000000	3.669285
H	0.000000	0.760776	4.257524
H	0.000000	-0.760776	4.257524

MP2/haTZ optimized structure

TABLE S18. Cartesian coordinates (in Å) of the C_4H_2/H_2O OH $\cdots\pi$ structure.

H	-1.314049	2.276889	0.013736
C	-0.492540	1.600941	0.009350
C	0.445608	0.819324	0.001580
C	1.493607	-0.061207	-0.005290
H	-1.733618	-0.477669	-0.010867
O	-2.595640	-0.908214	-0.048714
H	-2.524046	-1.635004	0.576504
C	2.423887	-0.850590	-0.010924
H	3.236320	-1.536312	-0.018138

MP2/haTZ optimized structure

TABLE S19. Cartesian coordinates (in Å) of the C_4H_2/H_2O $OH_2 \cdots \pi$ structure.

O	0.395334	0.000000	-0.229391
C	0.490202	0.000000	3.114601
C	-0.729898	0.000000	3.160143
H	1.552962	0.000000	3.071533
C	-2.097989	0.000000	3.203451
H	0.119669	-0.752777	0.302629
H	0.119669	0.752777	0.302629
C	-3.317680	0.000000	3.236701
H	-4.380409	0.000000	3.267118

MP2/haTZ optimized structure

TABLE S20. Cartesian coordinates (in Å) of the C_2H_4/H_2O OH $\cdots\pi$ structure.

C	0.036390	-0.014617	0.082319
C	0.036390	-0.014617	1.417680
H	0.936704	0.192243	-0.479498
H	0.936704	0.192243	1.979498
H	-0.864643	-0.217835	1.979749
H	-0.864643	-0.217835	-0.479749
H	0.008639	-2.387011	0.750000
O	-0.265437	-3.312581	0.750000
H	0.559759	-3.805475	0.750000

MP2/haTZ optimized structure

TABLE S21. Cartesian coordinates (in Å) of the C_2H_4/H_2O $CH_2 \cdots$ O structure.

C	0.000000	0.000000	-0.191995
C	0.000000	0.000000	1.141803
H	0.923018	0.000000	-0.755202
H	0.918767	0.000000	1.710605
H	-0.918767	0.000000	1.710605
H	-0.923018	0.000000	-0.755202
O	0.000000	0.000000	4.523124
H	0.000000	-0.758415	5.114499
H	0.000000	0.758415	5.114499

MP2/haTZ optimized structure

TABLE S22. Cartesian coordinates (in Å) of the C_2H_4/H_2O $CH_2 \cdots$ O(π) structure.

O	0.000000	0.000000	0.010224
C	0.666913	0.000000	3.387654
C	-0.666913	0.000000	3.387654
H	1.230216	0.000000	4.310928
H	1.216597	0.000000	2.457156
H	-1.230216	0.000000	4.310928
H	-1.216597	0.000000	2.457156
H	0.000000	-0.758888	-0.580682
H	0.000000	0.758888	-0.580682

MP2/haTZ optimized structure

TABLE S23. Cartesian coordinates (in Å) of the C_4H_6/H_2O CH $\cdots$ O structure.

C	0.776217	-0.496391	0.000000
C	0.000000	0.597981	0.000000
C	0.520307	1.954501	0.000000
C	-0.253411	3.050379	0.000000
H	-1.080044	0.487387	0.000000
H	1.600508	2.063671	0.000000
H	-1.332865	2.967544	0.000000
H	1.855285	-0.400157	0.000000
H	0.174178	4.042662	0.000000
H	0.354978	-1.491870	0.000000
O	-0.729620	-3.725420	0.000000
H	-1.673574	-3.909127	0.000000
H	-0.320189	-4.595578	0.000000

MP2/haTZ optimized structure

TABLE S24. Cartesian coordinates (in Å) of the C_4H_6/H_2O $CH_2 \cdots$ O structure.

C	0.792632	0.000000	-0.287325
C	0.334343	0.000000	0.973612
C	1.198851	0.000000	2.141155
C	0.743962	0.000000	3.403390
H	-0.737455	0.000000	1.141379
H	2.269498	0.000000	1.960251
H	-0.318935	0.000000	3.608952
H	1.856159	0.000000	-0.492670
H	1.419539	0.000000	4.246756
H	0.107882	0.000000	-1.122762
O	-2.617561	0.000000	-0.732590
H	-3.167621	-0.758984	-0.948535
H	-3.167621	0.758984	-0.948535

MP2/haTZ optimized structure

TABLE S25. Cartesian coordinates (in Å) of the C_4H_6/H_2O OH$\cdots\pi$ structure.

C	-0.428084	1.863830	0.128093
C	0.371537	0.915804	-0.386876
C	1.020450	-0.108737	0.414714
C	1.784663	-1.080277	-0.107342
H	0.549803	0.888976	-1.457365
H	0.859154	-0.069748	1.487429
H	1.958452	-1.137158	-1.174420
H	-0.619780	1.910481	1.192745
H	2.251482	-1.826951	0.518819
H	-0.895836	2.607715	-0.500667
O	-2.175679	-1.221161	-0.031697
H	-1.779639	-0.347303	-0.131509
H	-1.409591	-1.800446	0.027002

MP2/haTZ optimized structure

TABLE S26. Cartesian coordinates (in Å) of the C_4H_4/H_2O CH $\cdots$ O(p) structure.

C	0.358332	1.503826	0.000000
C	-1.146961	1.940734	0.000000
C	-1.518077	0.649569	0.000000
C	-0.011117	0.211552	0.000000
H	1.303916	2.024504	0.000000
H	0.505934	-0.736706	0.000000
H	-2.465284	0.131746	0.000000
H	-1.671425	2.884250	0.000000
O	1.555773	-2.916472	0.000000
H	2.510644	-3.030926	0.000000
H	1.209984	-3.813819	0.000000

MP2/haTZ optimized structure

TABLE S27. Cartesian coordinates (in Å) of the C_4H_4/H_2O CH $\cdots$ O structure.

C	-0.280201	1.530851	0.000000
C	1.251266	1.864827	0.000000
C	1.533960	0.551408	0.000000
C	0.000941	0.216397	0.000000
H	-1.188601	2.114045	0.000000
H	-0.579666	-0.694314	0.000000
H	2.443484	-0.030027	0.000000
H	1.838464	2.770643	0.000000
O	-1.671951	-2.830102	0.000000
H	-2.075060	-3.261233	0.759308
H	-2.075060	-3.261233	-0.759308

MP2/haTZ optimized structure

TABLE S28. Cartesian coordinates (in Å) of the C_4H_4/H_2O OH $\cdots\pi$ structure.

C	0.014331	-0.000606	-0.001554
C	0.014331	-0.000606	1.341554
C	1.577568	0.119215	1.342902
C	1.577568	0.119215	-0.002902
H	-0.743319	-0.075251	-0.765703
H	2.338658	0.202715	-0.764122
H	2.338658	0.202715	2.104122
H	-0.743319	-0.075251	2.105703
O	1.481060	-3.129010	0.670000
H	1.647664	-2.177004	0.670000
H	2.359436	-3.519937	0.670000

MP2/haTZ optimized structure

TABLE S29. Cartesian coordinates (in Å) of the C_4H_4/H_2O $OH_2 \cdots \pi$ structure.

C	0.015815	-0.041190	-0.002040
C	0.015815	-0.041190	1.342040
C	1.579004	0.076438	1.342723
C	1.579004	0.076438	-0.002723
H	-0.744760	-0.091744	-0.765922
H	2.339916	0.149171	-0.764858
H	2.339916	0.149171	2.104858
H	-0.744760	-0.091744	2.105922
O	1.429667	-3.165525	0.670000
H	1.698505	-2.237737	0.670000
H	0.469233	-3.115893	0.670000

MP2/haTZ optimized structure

TABLE S30. Cartesian coordinates (in Å) of the C_5H_6/H_2O CH $\cdots$ O structure.

C	-0.053103	0.000000	-0.262682
C	-0.172590	0.000000	1.230061
C	1.065751	0.000000	1.778068
C	2.057997	0.000000	0.705007
C	1.426442	0.000000	-0.492475
H	1.892054	0.000000	-1.466826
H	1.301494	0.000000	2.832851
H	3.128004	0.000000	0.856716
H	-1.111154	0.000000	1.764323
H	-0.532517	-0.877820	-0.708639
H	-0.532517	0.877820	-0.708639
O	2.410598	0.000000	5.018529
H	2.575673	0.759153	5.585440
H	2.575673	-0.759153	5.585440

MP2/haTZ optimized structure

TABLE S31. Cartesian coordinates (in Å) of the C_5H_6/H_2O OH $\cdots \pi$ structure.

C	-0.651418	0.255449	-1.194597
C	-0.852817	-1.045630	-0.483642
C	-0.811880	-0.833518	0.853675
C	-0.580738	0.587351	1.105515
C	-0.481501	1.238994	-0.079558
H	-0.315621	2.296880	-0.219111
H	-0.930107	-1.585531	1.620486
H	-0.505342	1.038247	2.084806
H	-1.010081	-1.992076	-0.979236
H	0.224488	0.230561	-1.850930
H	-1.511605	0.508271	-1.823399
O	2.531607	-0.120263	-0.045868
H	1.719500	0.292732	0.276577
H	2.343360	-1.060844	0.023948

MP2/haTZ optimized structure

TABLE S32. Cartesian coordinates (in Å) of the C_5H_6/H_2O $OH_2 \cdots \pi$ structure.

C	0.001178	0.142762	0.000925
C	0.000142	0.204801	1.496146
C	1.278066	0.298606	1.938013
C	2.182663	0.298604	0.790783
C	1.454918	0.204797	-0.348831
H	1.840188	0.188757	-1.357673
H	1.589427	0.366383	2.970626
H	3.259418	0.366379	0.852707
H	-0.891013	0.188764	2.106095
H	-0.469125	-0.773579	-0.369910
H	-0.551996	0.981257	-0.435257
O	1.097722	-2.938745	0.865563
H	1.680133	-2.352192	0.369560
H	0.751245	-2.352187	1.547597

MP2/haTZ optimized structure

TABLE S33. Cartesian coordinates (in Å) of the C_6H_6/H_2O CH $\cdots$ O structure.

C	-0.003738	0.460832	0.000000
C	-0.004457	-0.240614	1.205540
C	-0.005517	-1.635031	1.207034
C	-0.005894	-2.332945	0.000000
C	-0.005517	-1.635031	-1.207034
C	-0.004457	-0.240614	-1.205540
H	-0.001398	1.543378	0.000000
H	-0.004315	0.300111	2.143530
H	-0.006018	-2.176144	2.144705
H	-0.006587	-3.415490	0.000000
H	-0.006018	-2.176144	-2.144705
H	-0.004315	0.300111	-2.143530
O	0.099239	3.999575	0.000000
H	0.208490	4.580401	0.758735
H	0.208490	4.580401	-0.758735

MP2/haTZ optimized structure

TABLE S34. Cartesian coordinates (in Å) of the C_6H_6/H_2O CH $\cdots$ O(np) structure.

C	0.000000	0.000000	0.464142
C	-0.000000	1.205803	-0.236985
C	-0.000000	1.207168	-1.631437
C	0.000000	0.000000	-2.329239
C	-0.000000	-1.207168	-1.631437
C	-0.000000	-1.205803	-0.236985
H	0.000000	0.000000	1.546562
H	-0.000000	2.143261	0.304669
H	-0.000000	2.144747	-2.172739
H	0.000000	0.000000	-3.411811
H	-0.000000	-2.144747	-2.172739
H	-0.000000	-2.143261	0.304669
O	0.000000	0.000000	3.965191
H	0.759246	0.000000	4.555608
H	-0.759246	-0.000000	4.555608

MP2/haTZ optimized structure

TABLE S35. Cartesian coordinates (in Å) of the C_6H_6/H_2O CH $\cdots$ O(p) structure.

C	-0.000000	-0.000000	0.459958
C	-0.000000	1.205544	-0.241483
C	-0.000000	1.207037	-1.635900
C	0.000000	0.000000	-2.333810
C	-0.000000	-1.207037	-1.635900
C	-0.000000	-1.205544	-0.241483
H	-0.000000	-0.000000	1.542503
H	-0.000000	2.143518	0.299267
H	-0.000000	2.144696	-2.177035
H	0.000000	0.000000	-3.416356
H	-0.000000	-2.144696	-2.177035
H	-0.000000	-2.143518	0.299267
O	-0.000000	-0.000000	3.999075
H	0.000000	-0.758745	4.590072
H	0.000000	0.758745	4.590072

MP2/haTZ optimized structure

TABLE S36. Cartesian coordinates (in Å) of the C_6H_6/H_2O OH $\cdots \pi$ structure.

C	1.368111	0.000000	1.133918
C	0.670459	1.208583	1.134066
C	-0.724062	1.208165	1.133229
C	-1.420939	0.000000	1.132390
C	-0.724062	-1.208165	1.133229
C	0.670459	-1.208583	1.134066
H	2.450444	0.000000	1.136226
H	1.211850	2.145550	1.139634
H	-1.264896	2.145580	1.135578
H	-2.503435	-0.000000	1.130070
H	-1.264896	-2.145580	1.135578
H	1.211850	-2.145550	1.139634
O	0.304789	0.000000	4.437001
H	0.537418	0.000000	3.500241
H	-0.656706	0.000000	4.426429

MP2/haTZ optimized structure

TABLE S37. Cartesian coordinates (in Å) of the C_6H_6/H_2O $OH_2 \cdots \pi$ structure.

O	0.000000	0.000000	-0.221996
C	1.395185	-0.000489	3.050727
C	0.697174	1.207542	3.051984
C	-0.698016	1.208021	3.050727
C	-1.395185	0.000489	3.050727
C	-0.697174	-1.207542	3.051984
C	0.698016	-1.208021	3.050727
H	2.477432	-0.000603	3.049367
H	1.238482	2.145114	3.057967
H	-1.239239	2.145217	3.049367
H	-2.477432	0.000603	3.049367
H	-1.238482	-2.145114	3.057967
H	1.239239	-2.145217	3.049367
H	-0.375055	-0.649615	0.382461
H	0.375055	0.649615	0.382461

MP2/haTZ optimized structure

TABLE S38. Vibrational frequencies (in cm^{-1}) of the CH_4/H_2O OH $\cdots$ C structure.

Mode	MP2	B3LYP	B97-D	ωB97X-D	M06-2X
			A' Symmetry		
1	78.8	48.4	48.4	73.1	78.9
2	87.4	59.6	100.1	96.1	109.5
3	119.6	92.8	125.3	115.3	144.4
4	1358.8	1341.3	1304.7	1346.1	1344.2
5	1360.3	1343.6	1308.6	1348.5	1346.5
6	1588.1	1559.3	1517.3	1565.0	1564.1
7	1634.9	1630.5	1614.8	1640.1	1621.8
8	3064.8	3024.3	2929.9	3037.7	3054.6
9	3198.1	3125.5	3053.8	3153.9	3163.5
10	3206.6	3130.4	3060.8	3164.0	3177.0
11	3819.1	3796.1	3720.5	3873.9	3866.5
12	3944.7	3898.3	3830.5	3979.7	3968.6
			A" Symmetry		
13	26.3	29.0	41.5	−10.9	68.6
14	96.2	67.2	105.1	100.7	90.5
15	183.2	155.9	203.7	186.3	182.0
16	1357.2	1343.5	1308.4	1345.1	1341.0
17	1592.9	1561.4	1519.1	1569.1	1569.1
18	3200.2	3124.9	3050.6	3155.5	3167.4

TABLE S39. Vibrational frequencies (in cm^{-1}) of the CH_4/H_2O CH $\cdots$ O structure.

Mode	MP2	B3LYP	B97-D	ωB97X-D	M06-2X
			A' Symmetry		
1	39.1	−12.3	−35.2	14.1	34.2
2	65.2	43.0	50.5	41.6	81.4
3	86.3	80.6	74.7	79.0	121.2
4	1350.4	1336.0	1299.0	1336.8	1334.3
5	1362.1	1346.1	1309.6	1348.1	1346.2
6	1592.1	1561.0	1517.8	1566.3	1567.6
7	1629.2	1628.2	1611.6	1637.1	1620.2
8	3066.2	3024.3	2929.9	3038.6	3059.0
9	3200.2	3123.0	3049.6	3155.6	3170.7
10	3208.2	3134.6	3065.9	3164.0	3177.5
11	3821.3	3800.7	3724.4	3882.7	3871.2
			A" Symmetry		
12	11.9	15.7	−18.9	42.0	53.1
13	19.7	36.9	11.7	52.8	94.8
14	112.4	103.5	97.3	107.3	107.0
15	1363.8	1347.4	1311.1	1349.9	1347.7
16	1593.3	1561.8	1518.8	1566.9	1568.5
17	3199.7	3122.6	3049.1	3155.5	3170.0
18	3948.7	3903.6	3836.3	3990.6	3975.4

TABLE S40. Vibrational frequencies (in cm^{-1}) of the C_2H_6/H_2O CH $\cdots$ O structure.

Mode	MP2	B3LYP	B97-D	ωB97X-D	M06-2X
			A' Symmetry		
1	66.4	*a*	46.0	58.9	74.7
2	97.1	*a*	97.9	104.8	119.8
3	122.9	*a*	157.8	123.8	153.3
4	833.2	*a*	794.8	838.4	830.2
5	1024.9	*a*	948.8	1013.2	1017.8
6	1230.9	*a*	1191.3	1229.0	1224.5
7	1412.1	*a*	1366.1	1411.5	1404.4
8	1434.0	*a*	1379.3	1435.4	1427.5
9	1526.2	*a*	1460.6	1512.3	1510.6
10	1535.0	*a*	1473.6	1521.1	1520.4
11	1628.9	*a*	1612.4	1637.6	1617.1
12	3062.4	*a*	2930.9	3036.6	3049.1
13	3078.1	*a*	2948.4	3053.6	3068.8
14	3147.1	*a*	3007.5	3108.1	3120.7
15	3172.2	*a*	3034.4	3132.9	3145.7
16	3814.6	*a*	3722.0	3871.2	3862.2
17	3940.6	*a*	3831.4	3977.8	3964.1
			A" Symmetry		
18	64.2	*a*	44.7	31.0	99.0
19	102.9	*a*	103.3	100.3	119.3
20	168.9	*a*	191.4	163.3	184.0
21	335.6	*a*	320.4	334.1	344.0
22	828.7	*a*	791.8	832.8	824.5
23	1231.0	*a*	1190.5	1227.4	1223.1
24	1528.2	*a*	1461.0	1511.3	1511.0
25	1530.0	*a*	1469.7	1518.3	1517.1
26	3136.5	*a*	2994.1	3094.6	3104.3
27	3167.1	*a*	3027.8	3129.3	3140.4

[a] Collapses to different stationary point. (See text for details.)

TABLE S41. Vibrational frequencies (in cm^{-1}) of the C_2H_6/H_2O OH $\cdots$ C structure.

Mode	MP2	B3LYP	B97-D	ωB97X-D	M06-2X
			A' Symmetry		
1	44.2	15.3	13.1	40.5	51.2
2	75.3	51.8	106.4	80.4	81.8
3	113.7	93.6	119.4	88.6	111.1
4	839.6	831.7	796.6	843.4	838.8
5	1027.9	995.5	952.5	1016.9	1022.8
6	1235.9	1225.4	1191.5	1232.0	1229.5
7	1420.0	1415.1	1372.6	1417.3	1412.6
8	1436.2	1422.7	1378.3	1435.9	1429.8
9	1525.4	1504.1	1459.5	1510.1	1510.1
10	1529.7	1508.4	1470.5	1513.4	1513.2
11	1632.3	1630.1	1614.8	1638.4	1618.2
12	3062.6	3017.1	2931.7	3037.1	3049.9
13	3078.5	3030.1	2947.0	3054.1	3070.2
14	3142.3	3069.0	3005.1	3102.4	3112.0
15	3170.0	3096.0	3031.2	3131.8	3144.3
16	3817.0	3794.9	3720.2	3873.5	3865.1
17	3942.4	3897.0	3829.4	3979.1	3967.1
			A" Symmetry		
18	19.4	34.6	38.6	28.0	40.9
19	51.0	37.3	70.8	49.1	62.4
20	185.6	154.2	208.8	165.8	178.3
21	315.3	303.2	296.1	306.6	309.0
22	841.1	836.8	811.4	845.9	840.5
23	1236.5	1229.6	1201.5	1233.7	1229.5
24	1525.5	1504.1	1458.8	1510.7	1509.8
25	1530.3	1506.9	1464.0	1513.9	1513.1
26	3144.9	3065.9	2999.3	3102.4	3115.1
27	3170.1	3094.4	3028.8	3130.7	3143.2

TABLE S42. Vibrational frequencies (in cm^{-1}) of the C_2H_2/H_2O CH $\cdots$ O structure.

Mode	MP2	B3LYP	B97-D	ωB97X-D	M06-2X
			A' Symmetry		
1	49.0	58.5	65.2	77.2	89.5
2	101.9	108.6	102.6	130.3	121.5
3	116.9	109.6	142.8	157.9	141.9
4	628.3	680.3	627.3	707.4	719.5
5	796.7	815.5	783.5	833.3	833.8
6	1630.6	1629.4	1612.5	1637.1	1621.0
7	1958.8	2056.8	1999.4	2076.3	2091.6
8	3391.1	3364.4	3320.4	3360.6	3378.1
9	3505.1	3491.1	3435.6	3500.1	3511.0
10	3821.2	3801.3	3725.2	3879.6	3869.8
			A" Symmetry		
11	61.0	66.2	56.4	68.8	70.9
12	187.1	193.9	187.1	213.1	198.2
13	633.6	683.8	631.3	709.7	724.9
14	814.4	832.6	795.2	851.1	853.4
15	3946.9	3903.0	3835.6	3985.9	3973.0

TABLE S43. Vibrational frequencies (in cm^{-1}) of the C_2H_2/H_2O CH $\cdots$ O(p) structure.

Mode	MP2	B3LYP	B97-D	ωB97X-D	M06-2X
			A1 Symmetry		
1	117.3	108.8	105.4	124.0	121.7
2	1630.4	1629.3	1611.5	1637.3	1620.8
3	1959.0	2057.1	2001.0	2077.9	2091.4
4	3392.3	3366.6	3331.4	3367.9	3378.4
5	3505.4	3491.7	3439.5	3502.7	3510.7
6	3821.7	3802.6	3729.1	3885.2	3870.5
			B1 Symmetry		
7	−37.9	−44.7	−88.2	−75.4	89.8
8	95.7	98.8	82.0	101.0	118.3
9	627.7	679.7	624.4	706.5	720.4
10	795.3	813.5	776.7	827.3	833.9
			B2 Symmetry		
11	59.7	65.4	49.8	69.0	62.6
12	183.0	188.1	163.1	194.8	191.5
13	633.2	683.4	628.8	709.7	723.3
14	813.3	831.1	788.9	846.7	851.8
15	3947.7	3904.6	3840.4	3992.8	3974.0

TABLE S44. Vibrational frequencies (in cm^{-1}) of the C_2H_2/H_2O OH $\cdots\pi$ structure.

Mode	MP2	B3LYP	B97-D	ωB97X-D	M06-2X
			A' Symmetry		
1	114.0	96.9	132.0	109.4	124.3
2	189.1	184.2	162.5	167.2	159.2
3	756.2	769.7	748.6	781.2	791.6
4	766.2	779.3	756.6	789.1	798.6
5	1635.8	1633.2	1616.0	1642.2	1623.9
6	1964.4	2064.4	2004.9	2085.5	2097.9
7	3517.0	3506.8	3450.1	3520.2	3524.3
8	3782.9	3757.1	3689.6	3834.3	3838.8
9	3923.7	3879.3	3812.4	3960.8	3952.4
			A" Symmetry		
10	46.0	45.2	52.8	48.6	26.0
11	119.1	110.4	109.3	121.4	102.1
12	382.5	370.7	360.1	381.0	392.6
13	611.6	666.8	611.2	695.6	709.9
14	625.1	679.3	624.1	706.5	720.5
15	3428.9	3406.9	3353.5	3415.9	3417.9

TABLE S45. Vibrational frequencies (in cm^{-1}) of the C_2H_2/H_2O $OH_2 \cdots \pi$ structure.

Mode	MP2	B3LYP	B97-D	ωB97X-D	M06-2X
			A1 Symmetry		
1	87.3	67.6	87.1	109.8	112.0
2	759.6	773.0	751.7	783.8	793.3
3	1631.1	1631.9	1614.5	1646.7	1628.2
4	1964.6	2065.1	2005.8	2085.9	2098.1
5	3517.4	3507.6	3450.2	3520.4	3524.3
6	3823.5	3802.4	3724.5	3880.6	3871.2
			A2 Symmetry		
7	156.5	140.0	162.3	175.6	206.8
8	613.4	668.3	614.6	697.8	712.4
			B1 Symmetry		
9	−157.0	−155.0	−225.7	47.6	−59.1
10	758.0	771.0	751.7	783.1	793.9
11	3935.5	3892.5	3815.4	3973.3	3958.7
			B2 Symmetry		
12	23.3	23.3	32.6	38.7	16.2
13	297.2	274.9	324.4	314.9	342.9
14	616.5	671.6	616.6	700.6	714.2
15	3429.3	3407.8	3353.5	3416.2	3417.9

TABLE S46. Vibrational frequencies (in cm^{-1}) of the C_4H_2/H_2O CH $\cdots$ O structure.

Mode	MP2	B3LYP	B97-D	ωB97X-D	M06-2X
			A' Symmetry		
1	12.2	34.4	76.1	46.8	47.2
2	50.5	58.7	88.1	109.0	115.7
3	111.8	103.9	281.2	143.1	123.1
4	230.1	249.0	311.6	249.4	244.9
5	472.4	534.5	551.0	539.3	543.0
6	610.5	652.2	676.5	687.4	703.4
7	704.9	752.9	761.5	788.5	792.2
8	898.2	915.3	909.7	909.8	911.9
9	1631.1	1630.0	1643.3	1638.7	1621.7
10	1996.0	2104.2	2041.6	2137.6	2150.7
11	2181.6	2272.3	2215.9	2324.1	2330.8
12	3398.8	3383.7	3345.6	3376.5	3400.7
13	3478.7	3469.0	3418.0	3480.9	3486.0
14	3820.8	3802.1	3761.0	3880.8	3870.0
			A" Symmetry		
15	36.6	39.1	101.1	46.3	37.8
16	161.9	170.0	258.9	188.0	171.2
17	242.2	260.4	317.9	264.7	258.1
18	473.2	535.2	551.6	540.5	544.0
19	610.8	653.0	677.1	689.3	703.9
20	733.8	776.6	778.3	813.2	814.9
21	3946.2	3903.4	3856.8	3987.0	3972.9

TABLE S47. Vibrational frequencies (in cm^{-1}) of the C_4H_2/H_2O CH $\cdots$ O(p) structure.

Mode	MP2	B3LYP	B97-D	ωB97X-D	M06-2X
			A1 Symmetry		
1	111.8	103.8	88.9	113.9	115.7
2	898.2	915.3	901.8	910.1	911.9
3	1631.1	1630.0	1611.9	1638.3	1621.7
4	1996.0	2104.2	2037.6	2138.2	2150.7
5	2181.6	2272.4	2200.7	2324.5	2330.8
6	3398.9	3384.6	3355.9	3386.5	3400.7
7	3478.7	3469.0	3413.8	3481.0	3486.0
8	3820.9	3802.6	3729.6	3885.2	3870.0
			B1 Symmetry		
9	−9.2	−17.2	−85.5	−64.1	47.2
10	50.0	51.5	41.2	50.1	123.1
11	230.1	248.8	238.5	246.4	244.9
12	472.4	534.6	507.8	539.5	543.0
13	610.5	652.1	602.2	687.7	703.4
14	704.8	752.1	683.7	782.7	792.2
			B2 Symmetry		
15	36.6	39.1	30.6	41.0	37.8
16	161.7	168.6	149.3	172.9	171.2
17	242.2	260.1	246.1	260.0	258.1
18	473.2	535.3	508.0	540.4	544.0
19	610.8	652.9	602.9	688.3	703.9
20	733.7	775.9	702.8	807.0	814.9
21	3946.3	3904.0	3840.5	3992.2	3972.9

TABLE S48. Vibrational frequencies (in cm^{-1}) of the C_4H_2/H_2O OH $\cdots\pi$ structure.

Mode	MP2	B3LYP	B97-D	ωB97X-D	M06-2X
			A Symmetry		
1	17.3	16.7	22.5	19.8	*a*
2	58.8	63.4	62.2	78.7	*a*
3	100.7	80.6	119.1	103.2	*a*
4	176.2	163.4	153.4	160.1	*a*
5	217.7	230.2	229.0	230.2	*a*
6	221.3	238.8	230.9	237.0	*a*
7	297.5	277.6	298.8	307.3	*a*
8	464.3	531.0	504.2	536.3	*a*
9	467.4	532.6	507.6	538.5	*a*
10	622.4	665.3	617.3	700.5	*a*
11	629.2	670.1	617.7	704.3	*a*
12	629.9	672.7	622.7	707.2	*a*
13	636.2	676.7	624.0	710.3	*a*
14	897.6	914.9	902.0	909.8	*a*
15	1632.7	1631.0	1616.4	1642.9	*a*
16	2000.3	2109.6	2041.6	2144.5	*a*
17	2186.3	2278.0	2205.3	2331.5	*a*
18	3468.0	3459.1	3406.7	3472.2	*a*
19	3474.7	3465.7	3410.8	3477.7	*a*
20	3790.5	3772.9	3699.2	3848.6	*a*
21	3926.2	3884.7	3816.4	3965.8	*a*

[a] Collapses to different stationary point. (See text for details.)

TABLE S49. Vibrational frequencies (in cm^{-1}) of the C_4H_2/H_2O $OH_2 \cdots \pi$ structure.

Mode	MP2	B3LYP	B97-D	ωB97X-D	M06-2X
			A' Symmetry		
1	5.9	*a*	15.5	−8.1	*a*
2	83.1	*a*	89.1	101.7	*a*
3	206.4	*a*	224.6	218.3	*a*
4	246.9	*a*	273.4	271.2	*a*
5	465.3	*a*	504.7	536.1	*a*
6	625.4	*a*	618.3	696.4	*a*
7	629.6	*a*	619.3	702.6	*a*
8	897.6	*a*	902.1	909.4	*a*
9	1630.7	*a*	1616.5	1643.5	*a*
10	2000.4	*a*	2041.3	2143.1	*a*
11	2186.1	*a*	2204.6	2329.8	*a*
12	3469.8	*a*	3407.5	3470.1	*a*
13	3474.6	*a*	3411.0	3477.7	*a*
14	3820.0	*a*	3724.0	3875.0	*a*
			A" Symmetry		
15	−123.4	*a*	−137.7	−42.2	*a*
16	127.3	*a*	136.0	176.1	*a*
17	221.3	*a*	233.0	242.2	*a*
18	465.7	*a*	505.2	537.7	*a*
19	623.8	*a*	619.8	701.0	*a*
20	630.8	*a*	620.7	718.5	*a*
21	3935.9	*a*	3820.9	3973.5	*a*

[a] Collapses to different stationary point. (See text for details.)

TABLE S50. Vibrational frequencies (in cm^{-1}) of the C_2H_4/H_2O OH $\cdots\pi$ structure.

Mode	MP2	B3LYP	B97-D	ωB97X-D	M06-2X
			A' Symmetry		
1	72.3	81.8	67.3	84.6	69.6
2	111.7	94.7	130.1	109.5	129.2
3	245.8	232.6	227.5	239.1	256.5
4	826.8	835.5	801.4	841.3	834.7
5	992.1	992.6	962.8	1014.0	1008.3
6	1379.9	1380.3	1336.8	1390.6	1388.1
7	1637.0	1634.8	1617.2	1644.8	1620.5
8	1672.6	1684.3	1636.1	1707.6	1709.1
9	3189.3	3139.4	3069.0	3163.6	3167.5
10	3290.1	3225.8	3163.5	3253.2	3256.5
11	3773.9	3752.1	3676.1	3826.2	3837.1
12	3922.0	3879.4	3809.9	3961.3	3954.1
			A" Symmetry		
13	47.0	45.5	53.9	64.2	79.5
14	80.5	67.9	72.4	90.7	138.8
15	353.1	335.2	338.2	350.3	336.0
16	965.5	995.0	955.9	1003.8	1018.0
17	1075.3	1068.5	1042.9	1077.5	1078.6
18	1248.7	1246.9	1215.2	1250.7	1247.3
19	1482.8	1480.4	1439.7	1480.4	1476.8
20	3172.4	3126.9	3057.2	3146.3	3153.1
21	3263.3	3198.0	3136.5	3227.1	3230.8

TABLE S51. Vibrational frequencies (in cm^{-1}) of the C_2H_4/H_2O $CH_2 \cdots O$ structure.

Mode	MP2	B3LYP	B97-D	ωB97X-D	M06-2X
			A1 Symmetry		
1	64.3	34.2	32.9	62.6	67.4
2	1375.1	1376.4	1331.0	1387.8	1381.3
3	1478.3	1476.7	1434.2	1478.6	1470.7
4	1629.4	1628.6	1612.6	1637.7	1620.1
5	1675.5	1687.4	1638.8	1711.3	1712.5
6	3173.5	3125.5	3053.7	3145.6	3158.8
7	3195.1	3143.3	3072.3	3167.7	3177.7
8	3819.5	3800.2	3723.7	3881.8	3869.7
			A2 Symmetry		
9	81.3	69.2	68.4	92.8	119.0
10	1073.6	1066.4	1042.8	1075.5	1072.3
			B1 Symmetry		
11	−34.4	−9.3	−35.8	7.6	12.9
12	68.2	69.9	57.1	73.6	81.5
13	955.3	975.2	940.3	988.1	988.1
14	991.9	998.2	965.3	1016.1	1017.3
15	3946.6	3902.8	3835.1	3989.3	3973.8
			B2 Symmetry		
16	−26.6	−38.8	−54.0	28.7	29.3
17	96.1	70.3	72.2	84.2	144.7
18	815.8	825.8	787.1	835.9	820.9
19	1239.8	1239.3	1205.0	1244.9	1236.0
20	3262.1	3194.6	3131.2	3223.8	3234.1
21	3292.2	3225.6	3162.4	3253.3	3263.0

TABLE S52. Vibrational frequencies (in cm^{-1}) of the C_2H_4/H_2O $CH_2 \cdots O(\pi)$ structure.

Mode	MP2	B3LYP	B97-D	ωB97X-D	M06-2X
			A1 Symmetry		
1	79.0	50.4	61.4	67.3	76.8
2	827.3	836.5	802.9	841.5	827.1
3	1377.3	1378.0	1334.6	1386.6	1380.5
4	1628.0	1627.9	1611.0	1635.8	1617.6
5	1673.0	1685.3	1637.4	1708.6	1709.2
6	3188.3	3136.8	3066.1	3160.7	3170.7
7	3290.9	3224.9	3162.2	3252.2	3262.3
8	3818.1	3800.0	3724.0	3881.9	3868.4
			A2 Symmetry		
9	105.6	92.5	91.1	117.3	149.8
10	961.4	988.9	950.1	1007.5	1007.7
11	1077.6	1069.9	1046.6	1079.0	1076.6
			B1 Symmetry		
12	−60.0	−32.6	−62.5	−46.9	−65.3
13	173.3	154.6	152.5	166.6	170.7
14	983.3	982.6	953.6	993.3	994.0
15	3945.5	3902.7	3835.8	3990.0	3973.2
			B2 Symmetry		
16	57.1	−24.9	39.9	54.8	62.3
17	108.4	84.3	75.4	79.8	144.7
18	1250.6	1249.0	1217.9	1252.6	1245.4
19	1471.1	1470.7	1430.3	1469.1	1459.6
20	3170.8	3123.7	3053.6	3143.0	3156.1
21	3265.2	3197.7	3136.2	3227.0	3237.9

TABLE S53. Vibrational frequencies (in cm^{-1}) of the C_4H_6/H_2O CH $\cdots$ O structure.

Mode	MP2	B3LYP	B97-D	ωB97X-D	M06-2X
			A' Symmetry		
1	16.2	20.4	14.1	16.2	19.6
2	72.8	54.4	67.0	56.0	67.1
3	88.4	91.3	75.2	89.9	98.8
4	294.0	302.0	294.4	307.4	304.2
5	512.6	520.6	507.5	526.1	521.6
6	910.8	904.5	881.2	909.8	910.3
7	999.3	1010.1	981.8	1015.2	1005.7
8	1230.3	1229.1	1194.4	1235.6	1231.1
9	1311.4	1316.8	1280.7	1325.4	1317.7
10	1312.5	1322.7	1281.4	1328.5	1318.8
11	1419.9	1423.0	1382.2	1430.1	1425.5
12	1484.9	1483.3	1441.2	1486.6	1481.4
13	1629.9	1629.1	1600.1	1637.5	1620.5
14	1636.7	1650.4	1612.4	1679.5	1682.8
15	1699.3	1700.7	1647.4	1743.5	1743.6
16	3165.7	3121.0	3057.3	3144.2	3154.7
17	3169.5	3128.3	3061.0	3149.2	3159.6
18	3176.7	3132.5	3065.3	3156.6	3166.0
19	3181.8	3134.8	3069.9	3161.8	3170.9
20	3275.4	3219.3	3157.8	3243.5	3251.9
21	3275.6	3221.7	3165.9	3244.7	3253.9
22	3820.4	3800.6	3725.3	3882.0	3871.4
23	3947.1	3902.8	3836.8	3989.5	3975.5
			A" Symmetry		
24	−63.7	−56.8	−56.8	−58.8	−72.3
25	26.6	−27.1	−49.3	−26.6	48.3
26	51.9	44.3	42.1	49.7	62.0
27	167.9	176.2	177.4	166.2	170.6
28	548.1	549.1	534.5	552.6	554.9
29	784.5	789.0	766.5	798.2	799.1
30	926.6	937.4	898.0	956.7	961.2
31	954.4	963.6	925.3	981.8	985.7
32	993.8	1006.8	973.0	1023.0	1023.7
33	1053.0	1058.7	1030.7	1067.5	1067.9

TABLE S54. Vibrational frequencies (in cm^{-1}) of the C_4H_6/H_2O $CH_2 \cdots O$ structure.

Mode	MP2	B3LYP	B97-D	ωB97X-D	M06-2X
			A' Symmetry		
1	32.6	−11.1	17.7	40.1	38.1
2	78.8	51.1	62.8	69.2	79.6
3	114.0	89.5	76.6	88.4	108.4
4	290.1	295.7	289.8	307.3	300.8
5	510.2	518.5	505.5	525.6	518.7
6	907.4	902.3	878.5	909.5	906.1
7	995.0	1007.8	978.9	1014.9	1000.9
8	1227.3	1226.9	1192.5	1234.2	1227.0
9	1312.1	1317.4	1281.3	1326.7	1316.2
10	1313.2	1323.6	1286.0	1330.6	1318.4
11	1411.2	1416.0	1375.6	1424.8	1414.6
12	1474.3	1474.9	1433.6	1480.1	1469.2
13	1628.0	1628.0	1598.8	1635.6	1618.0
14	1634.5	1648.6	1611.4	1679.1	1679.9
15	1697.6	1699.7	1646.4	1743.6	1741.1
16	3168.7	3123.2	3058.8	3148.4	3157.4
17	3170.6	3131.3	3061.9	3150.1	3160.2
18	3178.8	3134.9	3066.4	3159.2	3166.4
19	3192.5	3142.6	3087.4	3171.7	3178.5
20	3274.9	3219.1	3157.4	3244.2	3252.8
21	3279.4	3224.5	3162.5	3248.1	3258.6
22	3816.9	3799.6	3724.1	3880.9	3867.8
			A" Symmetry		
23	−45.3	−16.0	−48.1	−29.4	−43.8
24	105.5	92.8	84.3	104.5	106.1
25	116.1	108.1	104.6	117.9	129.9
26	170.1	177.4	178.3	169.1	172.1
27	553.7	552.6	537.5	557.7	559.0
28	784.1	787.7	764.9	798.3	797.7
29	927.5	938.9	899.7	959.0	960.6
30	939.7	950.6	909.3	970.5	973.1
31	999.3	1010.8	979.5	1027.6	1025.6
32	1060.5	1064.7	1039.7	1075.1	1073.8
33	3944.2	3902.1	3835.8	3989.0	3972.6

TABLE S55. Vibrational frequencies (in cm^{-1}) of the C_4H_6/H_2O OH $\cdots\pi$ structure.

Mode	MP2	B3LYP	B97-D	ωB97X-D	M06-2X
			A Symmetry		
1	23.1	−91.5	26.1	−113.0	27.3
2	52.3	−13.6	73.4	46.3	72.7
3	105.3	67.7	120.3	89.4	118.8
4	150.7	79.2	170.3	103.8	163.3
5	175.5	147.5	183.6	166.5	175.6
6	191.7	212.3	227.1	206.2	216.0
7	289.3	275.5	290.7	302.7	299.9
8	345.9	348.9	344.0	316.9	320.3
9	510.3	508.1	505.5	524.5	519.4
10	547.8	543.6	534.7	552.2	553.8
11	783.4	783.7	766.8	798.4	798.0
12	905.7	906.3	876.8	905.7	905.2
13	941.5	948.1	915.5	972.6	974.9
14	942.7	949.2	916.5	975.3	978.3
15	995.4	996.0	977.2	1012.8	1002.9
16	997.8	1002.3	979.2	1025.1	1024.6
17	1056.7	1061.1	1034.2	1070.0	1069.8
18	1230.0	1232.2	1194.3	1235.3	1230.3
19	1313.0	1319.3	1283.3	1327.5	1319.6
20	1314.5	1319.5	1284.6	1330.9	1321.1
21	1415.7	1425.0	1379.6	1426.7	1421.7
22	1479.7	1485.1	1437.7	1482.6	1476.5
23	1633.1	1627.1	1599.1	1647.3	1632.6
24	1638.3	1658.4	1630.3	1677.9	1679.5
25	1696.4	1723.0	1646.9	1741.7	1740.2
26	3171.0	3167.4	3064.1	3151.7	3160.1
27	3173.1	3171.3	3066.8	3154.2	3163.2
28	3180.5	3177.6	3071.6	3162.0	3168.7
29	3186.0	3182.0	3078.8	3167.7	3174.4
30	3277.7	3270.8	3163.0	3248.4	3255.1
31	3278.0	3271.0	3163.2	3248.5	3255.5
32	3789.8	3771.8	3702.5	3859.9	3853.8
33	3911.0	3922.2	3788.2	3944.9	3938.4

TABLE S56. Vibrational frequencies (in cm^{-1}) of the C_4H_4/H_2O CH $\cdots$ O(p) structure.

Mode	MP2	B3LYP	B97-D	ωB97X-D	M06-2X
			A' Symmetry		
1	23.4	27.6	24.2	36.1	30.1
2	75.0	60.0	72.0	74.8	71.5
3	105.2	106.7	90.3	104.5	112.3
4	722.7	700.3	680.8	738.8	746.7
5	847.0	851.8	822.5	857.1	838.4
6	969.5	953.8	937.6	973.2	973.1
7	1061.0	1066.7	1039.8	1072.0	1069.2
8	1124.8	1115.4	1079.9	1132.1	1132.1
9	1195.7	1201.9	1169.9	1210.5	1200.9
10	1267.7	1271.3	1233.4	1284.2	1279.2
11	1566.0	1621.2	1576.1	1636.9	1620.2
12	1574.7	1628.7	1585.5	1654.2	1661.2
13	1630.0	1629.3	1612.1	1662.1	1667.9
14	3230.1	3190.2	3127.6	3215.9	3219.3
15	3244.5	3205.7	3143.5	3230.4	3235.2
16	3264.8	3226.4	3165.0	3252.0	3256.9
17	3274.0	3235.3	3176.1	3262.5	3265.7
18	3820.1	3800.6	3725.3	3881.9	3871.2
19	3946.7	3902.9	3836.8	3989.6	3975.3
			A" Symmetry		
20	−57.1	−52.5	−61.7	−73.7	−67.4
21	14.2	−25.1	−49.1	−41.8	51.4
22	57.6	55.0	47.3	54.0	61.3
23	500.8	540.5	519.2	543.8	538.4
24	574.7	594.9	570.0	609.8	617.9
25	600.8	625.1	595.3	639.3	648.6
26	853.1	901.7	861.1	921.1	928.6
27	880.9	918.6	876.7	937.7	945.3

TABLE S57. Vibrational frequencies (in cm^{-1}) of the C_4H_4/H_2O CH $\cdots$ O structure.

Mode	MP2	B3LYP	B97-D	ωB97X-D	M06-2X
			A' Symmetry		
1	27.8	29.3	23.9	33.5	28.0
2	70.6	63.5	76.8	77.1	74.8
3	78.4	74.4	94.4	111.4	78.6
4	722.4	700.2	680.8	738.5	746.7
5	847.0	851.8	822.5	856.7	838.3
6	968.6	953.3	937.5	972.9	972.3
7	1059.3	1065.6	1039.3	1071.7	1067.1
8	1124.0	1114.8	1079.8	1131.9	1131.4
9	1194.0	1200.8	1169.5	1210.3	1198.8
10	1265.9	1270.2	1233.1	1284.0	1277.5
11	1565.5	1620.6	1575.4	1636.6	1618.1
12	1574.3	1628.3	1585.0	1653.9	1659.8
13	1629.2	1628.8	1612.2	1662.0	1666.8
14	3230.2	3190.1	3127.4	3213.9	3219.2
15	3244.6	3205.5	3142.3	3229.3	3235.2
16	3264.8	3226.2	3164.8	3250.2	3256.8
17	3274.0	3235.0	3173.3	3262.2	3265.7
18	3819.5	3800.1	3724.1	3879.0	3870.2
			A" Symmetry		
19	22.1	29.9	8.5	−28.1	3.7
20	54.9	51.2	48.3	46.5	47.8
21	117.4	121.7	119.4	135.7	120.1
22	504.3	542.1	520.6	545.7	540.0
23	575.9	596.8	571.9	612.0	619.6
24	608.1	631.0	602.0	646.0	654.4
25	855.6	902.4	861.9	922.2	929.0
26	887.0	924.1	883.1	944.3	950.8
27	3946.4	3902.5	3835.6	3986.1	3974.4

TABLE S58. Vibrational frequencies (in cm^{-1}) of the C_4H_4/H_2O OH $\cdots\pi$ structure.

Mode	MP2	B3LYP	B97-D	ωB97X-D	M06-2X
			A' Symmetry		
1	53.1	35.1	34.5	39.2	*a*
2	112.6	97.6	130.3	112.4	*a*
3	216.9	232.6	207.5	216.0	*a*
4	585.5	601.9	577.2	611.0	*a*
5	599.5	628.0	598.4	637.5	*a*
6	967.3	953.5	937.0	971.3	*a*
7	1054.7	1062.1	1035.2	1066.4	*a*
8	1121.6	1113.3	1077.2	1129.1	*a*
9	1560.9	1617.0	1571.3	1642.8	*a*
10	1573.3	1629.4	1585.4	1650.6	*a*
11	1633.9	1635.6	1615.6	1662.2	*a*
12	3268.0	3230.0	3168.3	3258.3	*a*
13	3282.6	3243.2	3181.2	3272.7	*a*
14	3755.3	3728.7	3653.7	3808.3	*a*
15	3913.0	3874.0	3804.1	3956.1	*a*
			A" Symmetry		
16	42.7	39.9	49.7	43.9	*a*
17	125.2	66.6	93.2	79.3	*a*
18	368.2	353.8	355.3	367.6	*a*
19	513.7	540.7	520.4	545.0	*a*
20	723.7	703.3	682.3	735.2	*a*
21	849.0	854.0	825.2	859.7	*a*
22	853.1	905.8	864.5	922.6	*a*
23	876.5	911.5	870.8	927.7	*a*
24	1189.5	1197.0	1165.0	1204.2	*a*
25	1261.0	1266.3	1228.3	1278.1	*a*
26	3234.4	3194.9	3132.9	3222.9	*a*
27	3252.5	3212.8	3150.2	3240.3	*a*

[a] Collapses to different stationary point. (See text for details.)

TABLE S59. Vibrational frequencies (in cm^{-1}) of the C_4H_4/H_2O $OH_2 \cdots \pi$ structure.

Mode	MP2	B3LYP	B97-D	ωB97X-D	M06-2X
			A' Symmetry		
1	54.0	24.0	112.0	95.3	70.4
2	124.3	97.6	149.6	130.6	118.9
3	195.2	242.2	187.8	210.8	132.9
4	589.3	603.1	583.3	614.0	613.6
5	601.4	629.6	602.1	639.4	643.1
6	967.4	953.0	937.5	971.2	970.4
7	1054.7	1062.6	1035.1	1066.2	1059.9
8	1121.6	1113.3	1077.6	1128.8	1127.7
9	1561.2	1617.6	1570.2	1647.4	1631.1
10	1571.1	1627.9	1581.8	1657.6	1656.4
11	1637.8	1637.0	1635.0	1659.5	1662.7
12	3269.6	3231.6	3170.4	3259.6	3264.6
13	3279.5	3241.4	3179.3	3270.3	3273.4
14	3765.8	3725.8	3692.8	3856.2	3853.4
15	3910.2	3873.8	3771.7	3943.0	3930.7
			A" Symmetry		
16	46.3	45.7	57.0	46.0	42.1
17	181.1	94.1	245.2	212.1	246.9
18	366.5	356.7	383.9	345.6	366.0
19	514.2	541.5	522.6	545.8	540.3
20	725.0	702.5	685.6	736.5	749.1
21	849.7	854.7	827.6	860.3	842.7
22	854.8	906.8	867.7	925.6	927.8
23	877.0	913.4	869.7	927.0	930.1
24	1189.7	1197.4	1165.4	1204.2	1191.4
25	1261.2	1267.1	1228.5	1277.9	1270.7
26	3235.7	3196.2	3134.8	3224.0	3227.7
27	3250.0	3211.6	3149.0	3238.3	3243.3

TABLE S60. Vibrational frequencies (in cm^{-1}) of the C_5H_6/H_2O CH $\cdots$ O structure.

Mode	MP2	B3LYP	B97-D	ωB97X-D	M06-2X
			A' Symmetry		
1	9.2	19.8	−16.8	−18.1	−18.1
2	69.7	54.2	61.6	52.3	68.4
3	71.9	57.6	75.7	106.7	80.5
4	808.9	818.1	794.8	820.0	815.0
5	811.1	819.5	796.3	822.2	817.1
6	941.7	924.3	892.7	938.0	938.5
7	986.2	968.7	934.2	979.9	978.3
8	1034.0	1014.0	986.8	1024.1	1023.2
9	1106.5	1115.0	1076.8	1121.1	1113.7
10	1127.1	1134.7	1096.4	1141.9	1133.8
11	1261.0	1266.5	1224.2	1280.5	1270.9
12	1319.9	1323.8	1282.9	1335.8	1326.5
13	1403.9	1401.5	1357.8	1410.8	1403.6
14	1417.2	1415.3	1371.3	1425.8	1419.2
15	1526.7	1545.9	1496.0	1584.0	1586.3
16	1605.1	1628.1	1584.5	1637.1	1617.3
17	1628.6	1634.1	1611.7	1667.3	1668.7
18	3056.1	3008.2	2932.4	3043.0	3051.2
19	3228.2	3189.7	3124.6	3210.4	3223.1
20	3236.9	3198.9	3135.1	3221.2	3232.0
21	3253.0	3215.1	3151.4	3238.1	3248.9
22	3259.8	3221.3	3157.4	3246.2	3254.8
23	3819.0	3800.2	3723.9	3880.1	3870.1
			A" Symmetry		
24	−7.6	18.5	−18.7	14.8	−38.1
25	60.3	53.8	45.4	66.9	71.8
26	99.1	101.0	100.4	130.1	95.5
27	335.0	353.6	336.6	350.2	344.1
28	517.9	530.5	512.8	535.3	531.8
29	686.8	689.1	666.4	693.8	690.4
30	708.9	719.2	687.0	733.3	735.0
31	910.3	923.5	889.4	930.5	926.5
32	951.1	967.0	930.4	984.9	987.8
33	978.3	991.8	958.0	1010.3	1006.3
34	1124.6	1125.0	1082.2	1136.1	1131.6
35	3099.3	3027.4	2962.4	3074.8	3080.2
36	3946.3	3902.9	3835.7	3987.6	3974.6

TABLE S61. Vibrational frequencies (in cm^{-1}) of the C_5H_6/H_2O OH $\cdots\pi$ structure.

Mode	MP2	B3LYP	B97-D	ωB97X-D	M06-2X
			A Symmetry		
1	55.4	23.8	*a*	*a*	*a*
2	71.2	36.1	*a*	*a*	*a*
3	122.1	96.3	*a*	*a*	*a*
4	148.3	101.8	*a*	*a*	*a*
5	180.2	199.9	*a*	*a*	*a*
6	331.2	349.2	*a*	*a*	*a*
7	395.2	374.9	*a*	*a*	*a*
8	519.8	530.9	*a*	*a*	*a*
9	688.0	689.9	*a*	*a*	*a*
10	717.6	727.8	*a*	*a*	*a*
11	808.3	818.6	*a*	*a*	*a*
12	814.0	821.4	*a*	*a*	*a*
13	910.5	921.8	*a*	*a*	*a*
14	941.1	924.2	*a*	*a*	*a*
15	951.2	968.5	*a*	*a*	*a*
16	956.9	969.3	*a*	*a*	*a*
17	988.3	973.5	*a*	*a*	*a*
18	1030.9	1011.4	*a*	*a*	*a*
19	1104.3	1113.4	*a*	*a*	*a*
20	1124.2	1128.8	*a*	*a*	*a*
21	1131.3	1132.0	*a*	*a*	*a*
22	1265.5	1270.6	*a*	*a*	*a*
23	1317.8	1321.2	*a*	*a*	*a*
24	1400.4	1399.1	*a*	*a*	*a*
25	1412.8	1412.8	*a*	*a*	*a*
26	1522.1	1543.9	*a*	*a*	*a*
27	1599.1	1629.7	*a*	*a*	*a*
28	1633.2	1633.9	*a*	*a*	*a*
29	3059.9	3014.0	*a*	*a*	*a*
30	3105.3	3035.0	*a*	*a*	*a*
31	3228.9	3190.7	*a*	*a*	*a*
32	3237.9	3200.9	*a*	*a*	*a*
33	3254.8	3218.8	*a*	*a*	*a*
34	3261.5	3224.7	*a*	*a*	*a*
35	3761.4	3738.6	*a*	*a*	*a*
36	3908.9	3875.2	*a*	*a*	*a*

[a] Collapses to different stationary point. (See text for details.)

TABLE S62. Vibrational frequencies (in cm^{-1}) of the C_5H_6/H_2O $OH_2 \cdots \pi$ structure.

Mode	MP2	B3LYP	B97-D	ωB97X-D	M06-2X
			A Symmetry		
1	−106.3	−94.9	69.6	69.1	86.2
2	74.8	46.1	95.8	88.8	94.7
3	99.6	78.8	145.7	107.6	98.5
4	116.3	90.3	153.2	125.5	139.8
5	223.7	189.6	227.4	230.6	260.6
6	325.9	305.0	331.2	349.4	339.5
7	356.9	355.3	374.4	375.5	385.2
8	519.2	530.3	514.6	536.1	533.9
9	688.3	689.7	668.3	695.7	691.2
10	717.6	726.4	698.2	741.7	744.9
11	807.9	818.6	795.9	821.7	816.3
12	813.7	821.1	798.6	822.9	818.3
13	910.4	921.5	889.6	930.8	922.9
14	940.9	924.0	893.7	937.3	937.4
15	951.7	968.4	933.4	982.1	981.0
16	956.3	971.1	935.4	986.7	986.3
17	988.5	971.4	938.2	990.0	991.9
18	1031.1	1011.5	984.9	1020.8	1020.6
19	1104.1	1112.9	1075.1	1118.4	1110.3
20	1124.0	1130.3	1090.4	1138.1	1130.9
21	1132.1	1131.4	1093.1	1143.5	1139.4
22	1265.9	1271.1	1231.1	1284.9	1274.1
23	1317.8	1321.0	1280.1	1333.6	1325.4
24	1400.6	1398.8	1351.7	1410.4	1397.3
25	1413.3	1412.5	1369.2	1426.6	1415.0
26	1521.8	1543.5	1493.7	1579.8	1581.3
27	1599.2	1629.8	1580.8	1649.4	1633.8
28	1635.4	1638.0	1634.2	1662.1	1663.3
29	3060.0	3014.2	2941.6	3048.8	3054.0
30	3105.4	3035.8	2976.2	3083.4	3086.0
31	3228.2	3190.6	3126.8	3216.5	3225.4
32	3237.0	3200.3	3136.8	3225.7	3234.3
33	3253.4	3217.7	3155.3	3243.0	3251.0
34	3260.4	3223.8	3161.1	3250.1	3257.4
35	3792.0	3786.2	3696.8	3857.3	3847.6
36	3894.7	3870.2	3776.2	3940.9	3925.7

TABLE S63. Vibrational frequencies (in cm^{-1}) of the C_6H_6/H_2O CH $\cdots$ O structure.

Mode	MP2	B3LYP	B97-D	ωB97X-D	M06-2X
			A' Symmetry		
1	21.9	19.2	*a*	*a*	31.8
2	53.7	49.3	*a*	*a*	60.8
3	68.4	50.2	*a*	*a*	106.1
4	400.3	416.0	*a*	*a*	413.1
5	605.4	621.9	*a*	*a*	617.4
6	654.6	697.6	*a*	*a*	700.7
7	692.7	722.9	*a*	*a*	713.5
8	869.5	878.3	*a*	*a*	891.6
9	979.4	998.9	*a*	*a*	1019.6
10	995.6	1013.4	*a*	*a*	1023.2
11	1010.4	1029.0	*a*	*a*	1031.7
12	1017.3	1031.7	*a*	*a*	1050.3
13	1190.7	1197.0	*a*	*a*	1071.3
14	1502.8	1515.6	*a*	*a*	1197.0
15	1630.1	1629.5	*a*	*a*	1522.4
16	1632.6	1633.1	*a*	*a*	1621.4
17	3190.8	3155.1	*a*	*a*	1665.1
18	3205.6	3167.8	*a*	*a*	3192.0
19	3222.3	3183.2	*a*	*a*	3203.3
20	3229.7	3191.0	*a*	*a*	3217.4
21	3819.2	3800.4	*a*	*a*	3225.4
22	3945.7	3902.4	*a*	*a*	3869.6
			A" Symmetry		
23	−68.0	−57.5	*a*	*a*	25.3
24	10.5	19.2	*a*	*a*	52.4
25	92.5	95.8	*a*	*a*	105.1
26	398.3	414.1	*a*	*a*	410.9
27	607.8	624.3	*a*	*a*	620.1
28	860.6	870.2	*a*	*a*	880.7
29	981.2	1006.1	*a*	*a*	1013.6
30	1058.2	1060.3	*a*	*a*	1075.2
31	1061.3	1062.8	*a*	*a*	1165.6
32	1167.3	1175.2	*a*	*a*	1206.9
33	1200.7	1204.6	*a*	*a*	1326.1
34	1373.0	1334.9	*a*	*a*	1384.2
35	1460.5	1391.2	*a*	*a*	1527.4
36	1507.6	1519.5	*a*	*a*	1665.4
37	1633.3	1633.7	*a*	*a*	3200.6
38	3201.4	3163.7	*a*	*a*	3216.0
39	3218.6	3179.8	*a*	*a*	3973.2

[a] Collapses to different stationary point. (See text for details.)

TABLE S64. Vibrational frequencies (in cm^{-1}) of the C_6H_6/H_2O CH $\cdots$ O(np) structure.

Mode	MP2	B3LYP	B97-D	ωB97X-D	M06-2X
			A1 Symmetry		
1	73.2	55.2	69.1	52.2	67.4
2	605.5	622.0	604.4	624.6	617.5
3	1010.3	1013.3	979.6	1028.1	1019.7
4	1017.4	1029.0	999.8	1032.1	1031.6
5	1058.0	1060.1	1024.3	1072.3	1071.2
6	1190.4	1196.8	1151.6	1206.6	1196.7
7	1502.6	1515.3	1469.9	1527.4	1522.1
8	1628.6	1628.2	1583.2	1636.7	1619.7
9	1632.5	1632.9	1611.1	1666.7	1664.9
10	3190.9	3155.2	3092.9	3181.7	3192.2
11	3206.1	3168.3	3106.7	3193.3	3204.0
12	3222.9	3183.6	3122.2	3208.3	3218.2
13	3230.4	3191.6	3134.9	3217.9	3225.7
14	3818.5	3800.2	3724.8	3882.5	3869.7
			A2 Symmetry		
15	69.2	62.7	60.3	87.6	126.7
16	399.2	414.6	402.5	416.7	411.4
17	861.7	871.1	842.4	883.8	881.6
18	982.3	999.7	964.7	1015.3	1014.3
			B1 Symmetry		
19	5.1	17.3	−13.7	20.5	21.6
20	101.0	101.1	84.7	107.8	111.4
21	402.5	417.4	405.0	419.7	414.6
22	660.8	699.7	675.6	707.0	702.8
23	695.3	724.7	705.2	729.7	715.9
24	872.6	880.9	851.5	894.3	894.2
25	980.4	1007.4	972.5	1023.4	1024.4
26	1003.7	1036.2	1001.5	1052.6	1054.0
27	3945.6	3902.7	3836.6	3990.4	3973.8
			B2 Symmetry		
28	−10.5	14.3	−16.0	−16.0	18.1
29	75.6	58.6	14.0	37.8	132.9
30	607.7	624.2	605.8	627.3	620.0
31	1060.2	1062.0	1026.1	1074.5	1074.2
32	1166.7	1174.8	1128.7	1178.3	1165.0
33	1198.5	1203.1	1158.1	1213.2	1205.2
34	1371.9	1334.8	1320.6	1339.1	1326.0
35	1460.4	1390.5	1346.4	1392.6	1383.2
36	1506.4	1518.8	1473.3	1530.8	1526.5
37	1632.9	1633.3	1583.5	1667.5	1665.1
38	3201.6	3163.9	3100.8	3191.0	3200.7
39	3218.7	3180.0	3116.1	3207.9	3216.0

TABLE S65. Vibrational frequencies (in cm^{-1}) of the C_6H_6/H_2O CH $\cdots$ O(p) structure.

Mode	MP2	B3LYP	B97-D	ωB97X-D	M06-2X
			A1 Symmetry		
1	68.4	49.7	62.6	50.4	60.8
2	605.4	621.9	604.2	624.7	617.4
3	1010.4	1013.4	979.7	1028.3	1019.7
4	1017.4	1029.0	999.8	1032.1	1031.7
5	1058.2	1060.3	1024.5	1072.5	1071.3
6	1190.7	1197.0	1151.9	1206.9	1197.0
7	1502.8	1515.5	1470.1	1527.6	1522.4
8	1630.1	1629.5	1583.4	1638.1	1621.4
9	1632.6	1633.1	1612.3	1667.0	1665.1
10	3190.8	3155.1	3092.7	3181.7	3192.0
11	3205.7	3167.9	3106.2	3193.3	3203.4
12	3222.3	3183.3	3122.0	3208.5	3217.5
13	3229.8	3191.2	3133.1	3218.1	3225.5
14	3819.2	3800.5	3724.9	3882.9	3870.1
			A2 Symmetry		
15	−68.2	−58.0	−58.4	−13.2	88.6
16	398.2	414.0	402.0	416.2	410.8
17	860.6	870.2	841.5	882.9	880.7
18	981.2	998.8	963.9	1014.5	1013.6
			B1 Symmetry		
19	21.1	5.3	−47.2	−29.3	32.7
20	51.9	41.5	30.6	36.3	122.7
21	400.2	416.0	403.7	418.1	413.1
22	654.3	697.6	673.6	704.6	700.7
23	692.7	722.8	703.7	727.8	713.3
24	869.5	878.2	849.1	891.3	891.6
25	979.3	1006.0	971.2	1022.0	1023.1
26	995.7	1031.6	997.4	1048.3	1050.3
			B2 Symmetry		
27	10.5	19.2	11.9	11.0	25.7
28	92.0	94.6	76.1	101.4	107.7
29	607.8	624.3	605.9	627.4	620.1
30	1061.3	1062.8	1027.0	1075.5	1075.2
31	1167.3	1175.2	1129.2	1178.9	1165.6
32	1200.7	1204.6	1159.9	1214.9	1206.9
33	1373.0	1334.9	1320.7	1339.2	1326.1
34	1460.5	1391.2	1347.2	1393.4	1384.2
35	1507.6	1519.5	1474.2	1531.6	1527.4
36	1633.3	1633.7	1583.9	1667.9	1665.4
37	3201.4	3163.7	3100.5	3190.9	3200.6
38	3218.6	3179.8	3115.8	3207.8	3216.0
39	3945.7	3902.6	3836.2	3990.1	3973.6

TABLE S66. Vibrational frequencies (in cm^{-1}) of the C_6H_6/H_2O OH $\cdots\pi$ structure.

Mode	MP2	B3LYP	B97-D	ωB97X-D	M06-2X
			A' Symmetry		
1	44.9	18.0	36.5	−54.3	69.9
2	101.5	71.9	109.1	78.0	111.0
3	134.1	161.3	133.4	141.7	158.2
4	402.3	415.5	403.4	418.1	414.1
5	605.8	622.9	605.1	626.1	618.2
6	687.9	699.1	675.4	705.7	701.8
7	693.4	724.7	705.2	733.4	727.1
8	867.8	876.8	848.2	889.9	890.8
9	983.9	1003.5	968.8	1019.6	1020.1
10	987.9	1013.0	979.5	1028.1	1020.5
11	1009.7	1028.2	995.1	1032.6	1030.6
12	1016.9	1031.5	1001.1	1046.7	1046.2
13	1057.7	1060.0	1024.6	1072.3	1070.8
14	1192.8	1198.7	1154.5	1209.3	1199.2
15	1502.0	1515.5	1470.3	1527.7	1521.6
16	1630.3	1632.1	1583.4	1650.0	1630.0
17	1632.9	1634.9	1618.5	1666.5	1663.7
18	3195.2	3160.0	3099.7	3187.6	3196.8
19	3207.3	3169.5	3108.9	3196.0	3205.4
20	3223.5	3184.6	3122.8	3212.3	3220.1
21	3233.7	3194.7	3133.0	3223.9	3230.1
22	3786.3	3773.0	3701.9	3862.2	3852.3
23	3919.0	3884.3	3815.8	3959.0	3945.4
			A" Symmetry		
24	19.0	−12.9	−11.5	54.4	62.8
25	53.5	40.7	40.9	85.9	93.1
26	224.2	233.6	236.8	268.7	270.4
27	399.5	413.8	401.2	416.0	411.0
28	605.5	622.8	604.6	625.8	618.1
29	866.1	874.6	846.3	887.7	885.6
30	981.6	1003.9	968.1	1019.0	1016.6
31	1058.5	1060.5	1025.2	1073.2	1072.6
32	1166.5	1174.6	1129.1	1178.5	1164.8
33	1192.2	1198.4	1153.9	1208.1	1199.9
34	1369.1	1333.9	1319.7	1338.4	1324.7
35	1461.0	1388.8	1345.0	1390.9	1381.1
36	1502.5	1515.9	1470.7	1528.0	1523.2
37	1629.8	1631.7	1582.0	1665.3	1661.8
38	3209.0	3170.6	3110.3	3199.4	3208.2
39	3225.3	3186.0	3124.6	3215.3	3222.5

TABLE S67. Vibrational frequencies (in cm^{-1}) of the C_6H_6/H_2O $OH_2 \cdots \pi$ structure.

Mode	MP2	B3LYP	B97-D	ωB97X-D	M06-2X
			A1 Symmetry		
1	100.9	57.4	109.3	109.2	125.9
2	403.6	415.1	403.3	418.5	414.6
3	605.8	623.0	605.0	626.0	618.1
4	692.2	698.4	674.5	705.4	701.4
5	981.7	1003.2	968.5	1019.6	1020.5
6	1009.5	1012.9	979.3	1028.0	1030.5
7	1192.9	1198.9	1154.7	1209.4	1199.3
8	1631.0	1632.8	1583.8	1650.1	1632.7
9	1635.6	1637.1	1629.9	1666.6	1663.8
10	3205.3	3168.2	3107.3	3195.4	3204.6
11	3232.7	3194.1	3132.5	3223.6	3229.7
12	3803.6	3796.7	3713.3	3869.8	3858.5
			A2 Symmetry		
13	18.7	16.3	−25.0	63.1	118.6
14	399.3	413.5	400.2	415.9	410.9
15	605.2	622.7	604.3	625.7	617.8
16	979.8	1003.3	967.8	1019.1	1016.5
17	1191.8	1198.0	1153.6	1208.0	1199.8
18	1369.2	1388.8	1345.1	1390.9	1381.1
19	1629.6	1631.7	1581.8	1665.3	1661.8
20	3208.4	3170.5	3110.6	3199.3	3208.0
			B1 Symmetry		
21	51.6	23.8	39.4	56.1	63.4
22	263.5	227.3	285.8	272.5	293.4
23	864.2	874.4	845.5	887.5	885.2
24	1058.4	1060.5	1025.4	1073.2	1072.6
25	1166.3	1174.5	1129.2	1178.5	1164.8
26	1461.9	1333.9	1320.1	1338.5	1324.9
27	1502.5	1515.8	1470.9	1528.0	1523.3
28	3224.8	3185.8	3124.8	3215.2	3222.3
			B2 Symmetry		
29	−114.5	−95.3	−24.9	59.1	67.0
30	68.1	48.7	69.5	121.7	109.5
31	686.9	723.9	705.0	733.5	727.0
32	866.6	875.9	848.5	890.1	890.9
33	979.1	1028.0	994.8	1032.4	1019.9
34	1016.5	1031.6	1001.4	1047.2	1045.7
35	1057.4	1059.8	1024.3	1072.2	1070.7
36	1502.0	1515.6	1470.4	1527.7	1521.6
37	3193.9	3159.3	3099.4	3187.3	3196.4
38	3221.9	3183.7	3121.9	3211.9	3219.6
39	3909.3	3885.5	3798.9	3956.7	3940.3