Electronic Supplementary Information

Structures and Hydrogen Bonding of 1,7-dioxaspiro[5.5]undecane and its Hydrates

Yugao Xu,[a] Zhi-You Wei,[b,c] Wenqin Li,[a] Jiaqi Zhang,[a] Tao Lu,[a] Yan Jin,[a] Wei-Jun Zheng,[b,c] and Gang Feng*[a]

[a] School of Chemistry and Chemical Engineering, Chongqing University, Daxuecheng South Rd. 55, 401331, Chongqing, China. E-mail: fengg@cqu.edu.cn

[b] Beijing National Laboratory for Molecular Sciences (BNLMS), State Key Laboratory of Molecular Reaction Dynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China.

[c] University of Chinese Academy of Sciences, Beijing 100049, China.

Table of Content:

Table S7. B3LYP-D3(BJ)/def2-TZVP calculated low energy isomers of the 1,7DSU···$(H_2O)_5$ cluster and their spectroscopic parameters.

Table S8. The result of NBO analysis for the most stable isomer of the 1,7DSU···H_2O cluster.

Table S9. The result of NBO analysis for the most stable isomer of the 1,7DSU···$(H_2O)_2$ cluster.

Table S10. The result of NBO analysis for the most stable isomer of the 1,7DSU···$(H_2O)_3$ cluster.

Table S11. The result of NBO analysis for the most stable isomer of the 1,7DSU···$(H_2O)_4$ cluster.

Table S12. The result of NBO analysis for the most stable isomer of the 1,7DSU···$(H_2O)_5$ cluster.

Table S13. Measured transition lines for the 1,7DSU.

Table S14. Measured transition lines for 1,7DSU···H_2O.

Table S15. Measured transition Lines for 1,7DSU···$H_2{}^{18}O$.

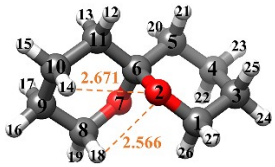
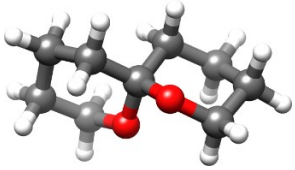
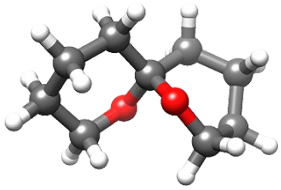
Table S16. Measured transition lines for 1,7DSU···D_2O.

Table S17. Measured transition lines for 1,7DSU···HDO.

Table S18. Measured transition lines for 1,7DSU···DHO cluster.

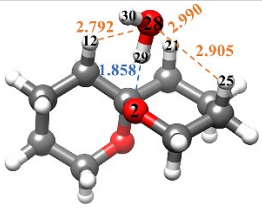
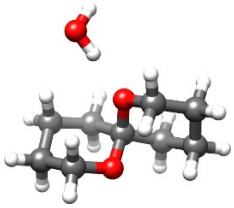
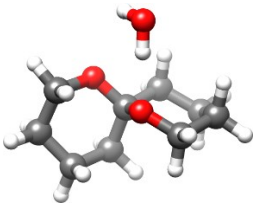
Table S19. Measured transition lines for 1,7DSU···$(H_2O)_2$.

Table S1: B3LYP-D3(BJ)/def2-TZVP calculated stable conformers of 1,7DSU and their spectroscopic parameters.

parameter	**m-1**	**m-2**	**m-3**
			
A, B, C [MHz]	2224, 837, 806	2227, 821, 789	2190, 873, 800
μ_a, μ_b, μ_c [D]	0.0, −0.02, 0.0	−0.5, −1.2, −1.2	0.0, −0.1, 0.06
ΔE [cm^{-1}][a]	0	1343	1741

[a] calculated at the MP2/aug-cc-PVTZ level on the top of the B3LYP-D3(BJ)/def2-TZVP geometry.

Table S2: B3LYP-D3(BJ)/def2-TZVP calculated low energy isomers of the 1,7DSU···H_2O cluster and their spectroscopic parameters.

parameter	**m-1/1w-1**	**m-1/1w-2**	**m-2/1w-3**
			
A, B, C [MHz]	1265, 753, 612	1132, 795, 608	1213, 787, 622
μ_a, μ_b, μ_c [D]	1.6, 0.4, 1.1	1.7, −1.1, −1.0	−1.0, −1.7, 3.7
ΔE [cm^{-1}][a]	0	109	1156

[a] calculated at the MP2/aug-cc-PVTZ level on the top of the B3LYP-D3(BJ)/def2-TZVP geometry.

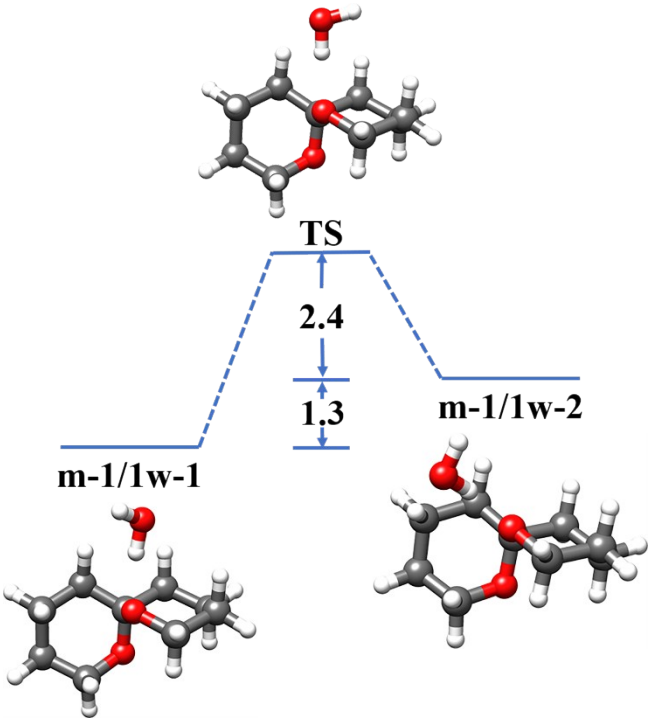
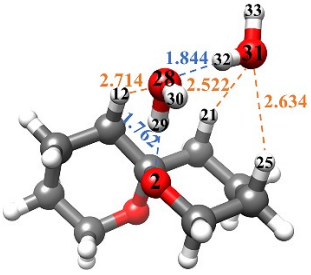
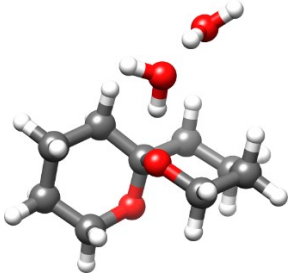
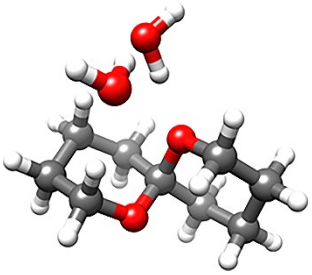
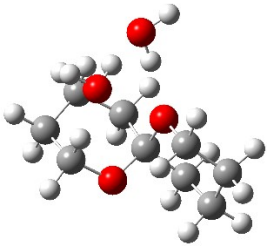
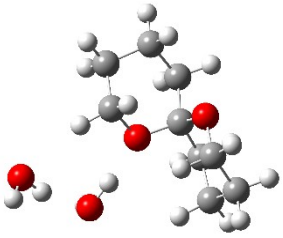
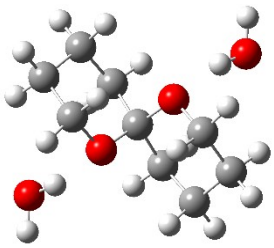


Figure S1. The interconversion of isomer **m-1/1w-2** to isomer **m-1/1w-1** calculated at the B3LYP-D3(BJ)/def2-TZVP level of theory. The MP2/aug-cc-pVTZ calculated relative energies based on the B3LYP-D3(BJ)/def2-TZVP geometries are given in kJ mol^{-1}.

Table S3. The experimental (r_s and r_0) and theoretical coordinates of the 1,7DSU···H_2O cluster.

	a (Å)			*b* (Å)			*c* (Å)		
	r_e	r_s	r_0	r_e	r_s	r_0	r_e	r_s	r_0
$H_2{}^{18}O$	−1.965	±1.9853(8)	−1.9211	−2.650	±2.7271(6)	−2.7588	0.108	0	0.088
DOH	−1.376	±1.312(1)	−1.3530	−1.940	±1.9245(8)	−2.0253	0.419	±0.401(4)	0.3858
HOD	−1.703	±2.0394(7)	−1.6199	−3.437	±3.2929(5)	−3.5341	0.594	±0.583(3)	0.5705

Table S4: B3LYP-D3(BJ)/def2-TZVP calculated low energy isomers of the 1,7DSU···$(H_2O)_2$ cluster and their spectroscopic parameters.

parameter	**m-1/2w-1**	**m-1/2w-2**	**m-1/2w-3**
			
A, B, C [MHz]	988, 583, 473	918, 600, 485	828, 658, 500
μ_a, μ_b, μ_c [D]	−1.2, 0.7, 1.4	1.3, −0.1, 1.5	−0.6, −0.1, 1.6
ΔE [cm^{-1}][a]	0	41	195
parameter	**m-1/2w-4**	**m-1/2w-5**	**m-1/2w-6**
			
A, B, C [MHz]	1007, 528, 432	808, 598, 434	946, 595, 492
μ_a, μ_b, μ_c [D]	−2.2, −0.3, 0.7	2.1, −0.1, −0.8	0, 0, −2.5
ΔE [cm^{-1}]	227	319	576

[a] calculated at the MP2/aug-cc-PVTZ level on the top of the B3LYP-D3(BJ)/def2-TZVP geometry.

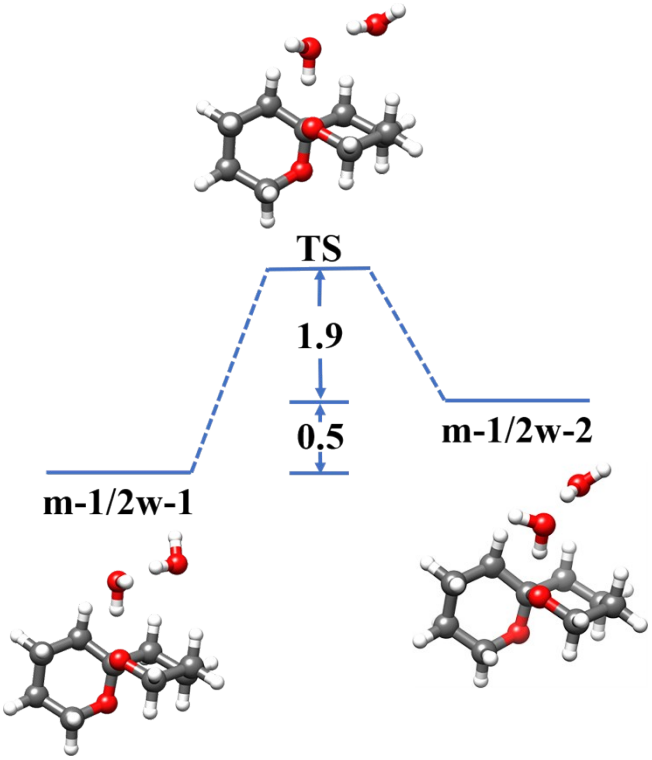
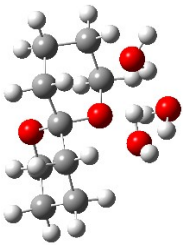
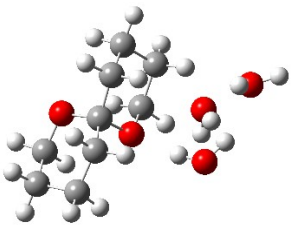
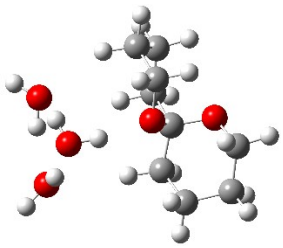
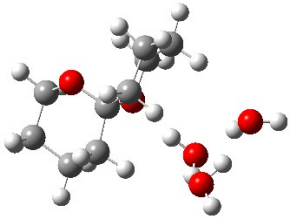
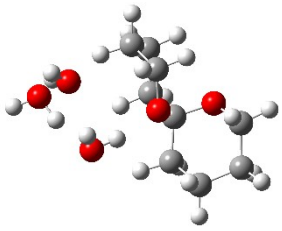
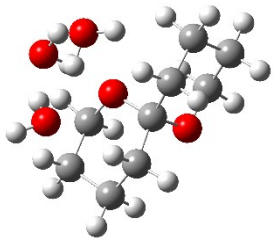
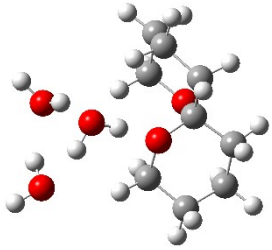
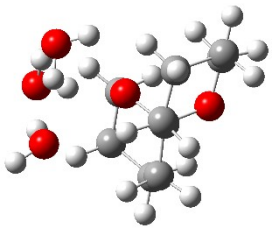
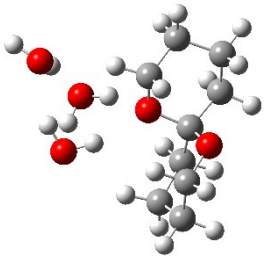
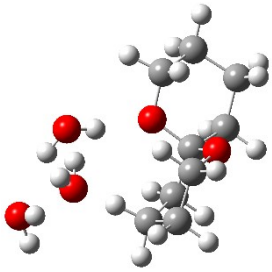
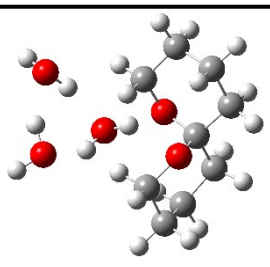
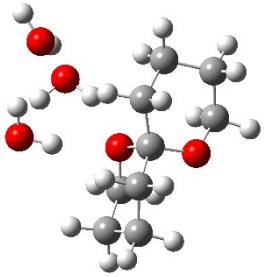
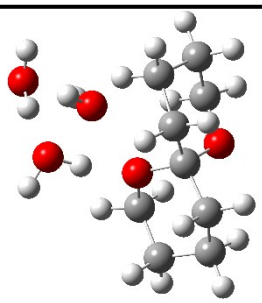
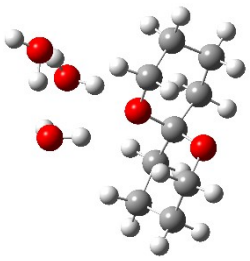
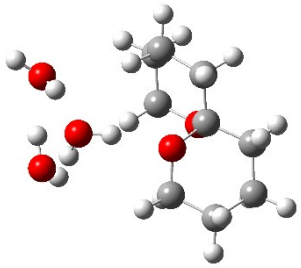
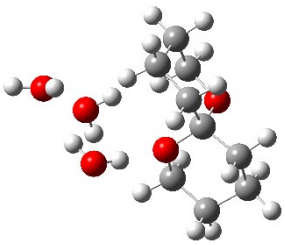
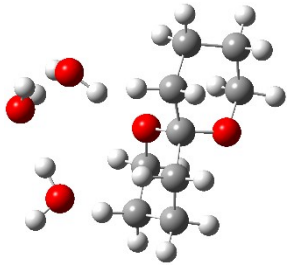
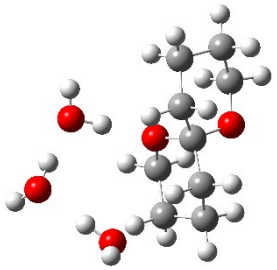
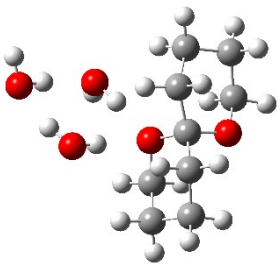
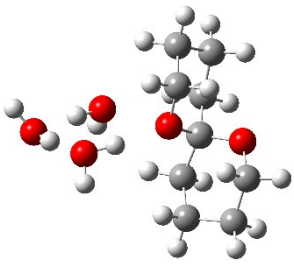
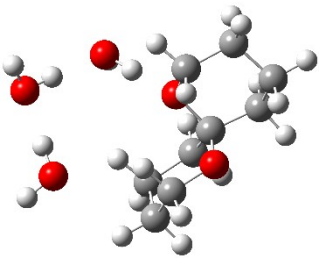


Figure S2. The interconversion of isomer **m-1/2w-2** to isomer **m-1/2w-1** explored using the synchronous transit-guided quasi-Newton (STQN) method and were further confirmed by transition state optimization at the B3LYP-D3(BJ)/def2-TZVP level of theory. The MP2/aug-cc-pVTZ calculated relative energies based on the B3LYP-D3(BJ)/def2-TZVP geometries are given in kJ mol^{-1}.

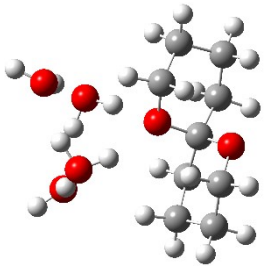
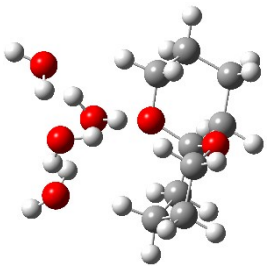
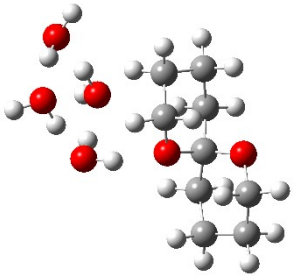
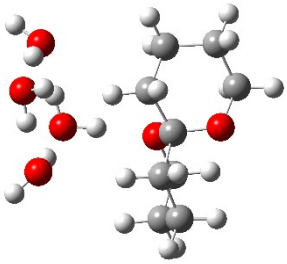
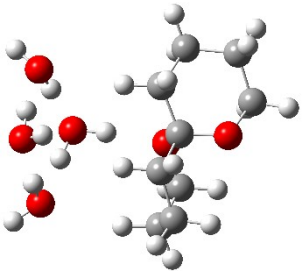
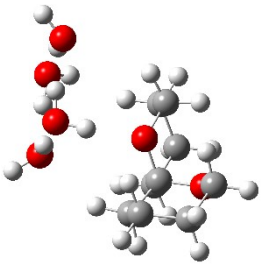
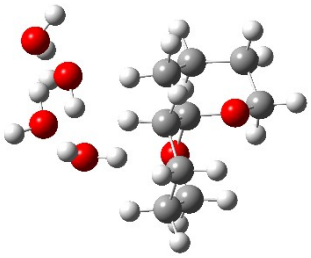
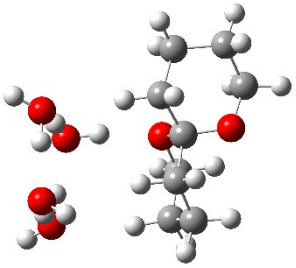
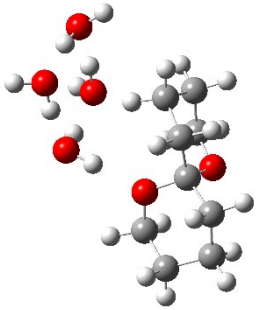
Table S5: B3LYP-D3(BJ)/def2-TZVP calculated low energy isomers of the 1,7DSU···$(H_2O)_3$ cluster and their spectroscopic parameters..

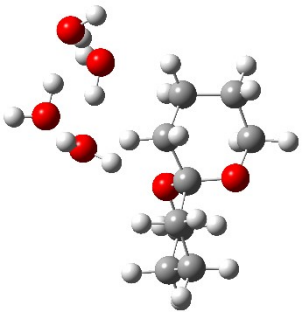
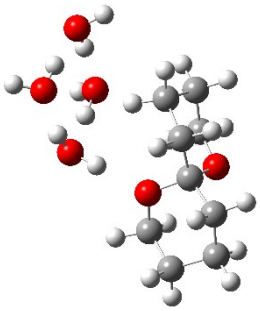
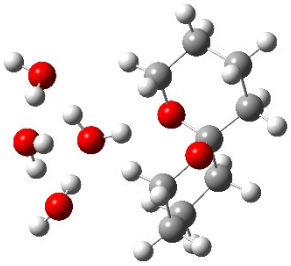
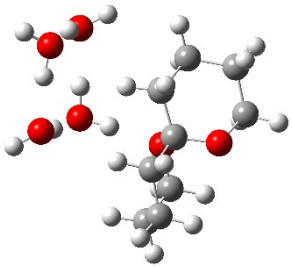
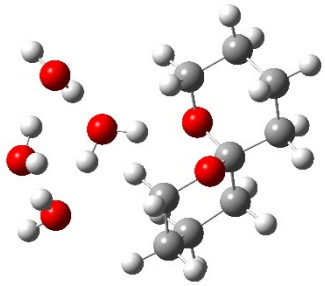
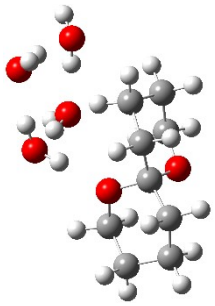
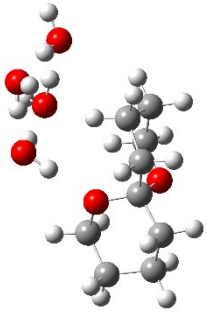
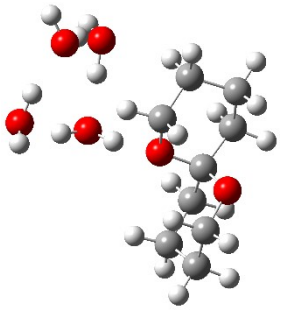
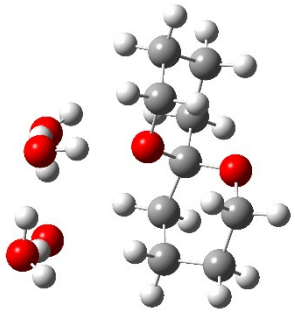
parameter	**m-1/3w-1**	**m-1/3w-2**	**m-1/3w-3**
			
A, B, C [MHz]	736, 490, 368	869, 429, 361	751, 479, 366
μ_a, μ_b, μ_c [D]	0.7, 0.2, −0.4	0.7, 0.3, −0.4	0.8, 0, 0.4
ΔE [cm^{-1}][a]	0	17	17
parameter	**m-1/3w-4**	**m-1/3w-5**	**m-1/3w-6**
			
A, B, C [MHz]	810, 455, 372	882, 400, 349	705, 496, 364
μ_a, μ_b, μ_c [D]	0.8, 0.3, −0.6	−0.8, 0, 0	−1.4, 0.2, 1.1
ΔE [cm^{-1}]	46	77	174
parameter	**m-1/3w-7**	**m-1/3w-8**	**m-1/3w-9**
			
A, B, C [MHz]	683, 512, 366	714, 461, 352	695, 527, 387
μ_a, μ_b, μ_c [D]	−0.9, −0.1, 0.7	2.0, −0.9, −0.9	−1.0, 1.7, −0.1
ΔE [cm^{-1}]	183	233	234
parameter	**m-1/3w-10**	**m-1/3w-11**	**m-1/3w-12**
			

A, B, C [MHz]	920, 393, 345	685, 496, 361	663, 568, 380
μ_a, μ_b, μ_c [D]	−1.3, −1.4, 0	0.9, −0.2, −0.5	−1.6, 1.6, −0.2
ΔE [cm^{-1}]	239	299	309
parameter	**m-1/3w-13**	**m-1/3w-14**	**m-1/3w-15**
			
A, B, C [MHz]	695, 496, 420	726, 503, 384	824, 447, 359
μ_a, μ_b, μ_c [D]	0.6, −0.6, 1.0	−1.4, 0.9, −1.4	−1.3, 1.0, 0.9
ΔE [cm^{-1}]	321	342	356
parameter	**m-1/3w-16**	**m-1/3w-17**	**m-1/3w-18**
			
A, B, C [MHz]	795, 412, 343	721, 479, 368	776, 435, 355
μ_a, μ_b, μ_c [D]	1.7, −1.5, 0	−1.0, 1.0, 1.3	−1.6, −1.5, −0.6
ΔE [cm^{-1}]	368	429	456
parameter	**m-1/3w-19**	**m-1/3w-20**	**m-1/3w-21**
			
A, B, C [MHz]	661, 523, 380	678, 459, 380	733, 454, 365
μ_a, μ_b, μ_c [D]	2.9, −2.2, 2.4	1.3, −1.2, 1.4	−1.3, 0.9, 1.4
ΔE [cm^{-1}]	491	502	576

[a] calculated at the MP2/aug-cc-PVTZ level on the top of the B3LYP-D3(BJ)/def2-TZVP geometry.

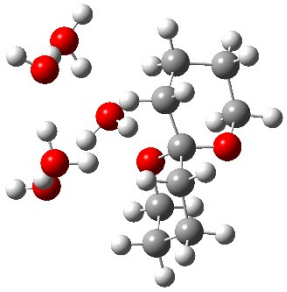
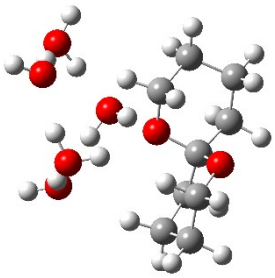
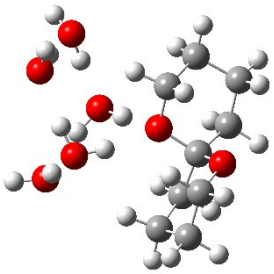
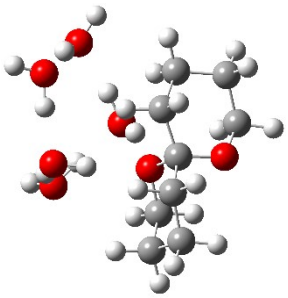
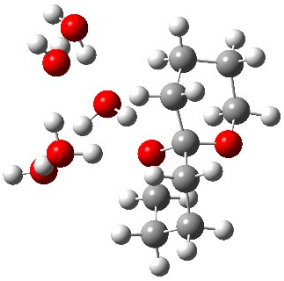
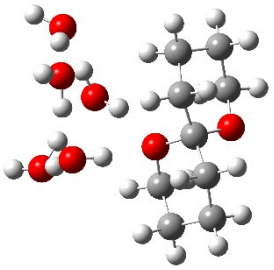
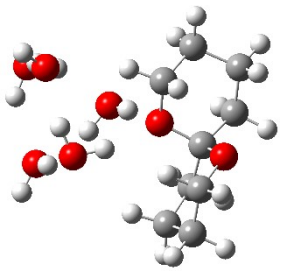
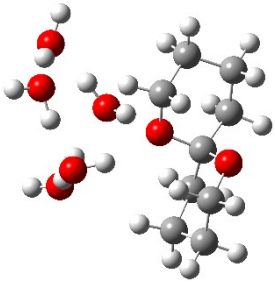
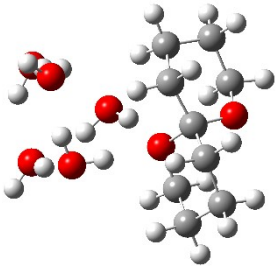
Table S6: B3LYP-D3(BJ)/def2-TZVP calculated low energy isomers of the 1,7DSU···$(H_2O)_4$ cluster and their spectroscopic parameters..

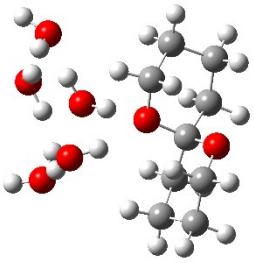
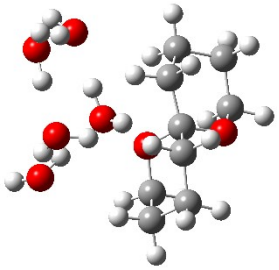
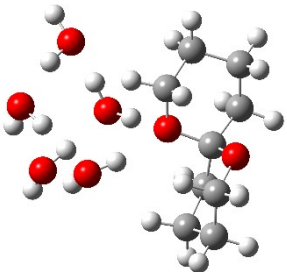
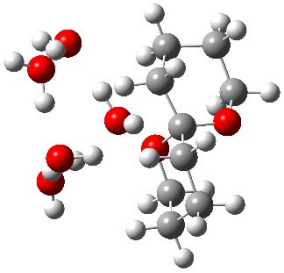
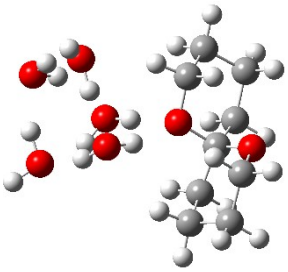
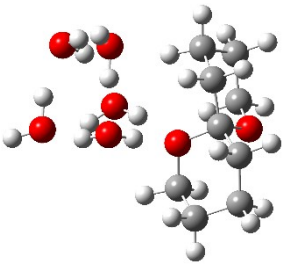
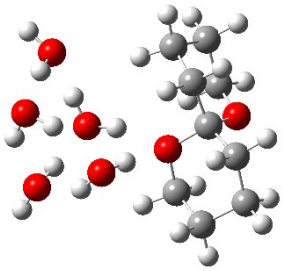
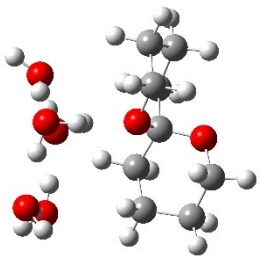
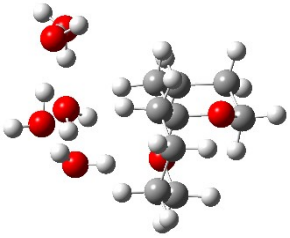
parameter	**m-1/4w-1**	**m-1/4w-2**	**m-1/4w-3**
			
A, *B*, *C* [MHz]	581, 456, 337	580, 451, 337	817, 305, 289
μ_a, μ_b, μ_c [D]	0.4, 0.0, −0.1	0.4, 0.0, −0.1	0.1, 0.6, 0
ΔE [cm^{-1}][a]	0	99	217
parameter	**m-1/4w-4**	**m-1/4w-5**	**m-1/4w-6**
			
A, *B*, *C* [MHz]	588, 407, 307	635, 385, 303	809, 309, 290
μ_a, μ_b, μ_c [D]	0.3, 0.0, 0.5	0.2, 0.1, 0.5	−0.1, 0.6, 0.3
ΔE [cm^{-1}]	237	240	254
parameter	**m-1/4w-7**	**m-1/4w-8**	**m-1/4w-9**
			
A, *B*, *C* [MHz]	589, 403, 307	662, 368, 298	785, 316, 289
μ_a, μ_b, μ_c [D]	−0.3, −0.2, 0.5	0.2, 0.2, −0.5	−0.5, −0.3, −0.1
ΔE [cm^{-1}]	279	323	346
parameter	**m-1/4w-10**	**m-1/4w-11**	**m-1/4w-12**

			
A, B, C [MHz]	670, 336, 290	784, 315, 288	610, 400, 304
μ_a, μ_b, μ_c [D]	0.6, 0.4, 0.2	0.6, −0.4, 0.1	0.1, −0.1, 0.6
ΔE [cm^{-1}]	379	388	404
parameter	**m-1/4w-13**	**m-1/4w-14**	**m-1/4w-15**
			
A, B, C [MHz]	589, 407, 309	652, 380, 299	762, 330, 299
μ_a, μ_b, μ_c [D]	0.5, 0.1, 1.1	−0.2, 0.0, −0.5	−0.1, 0.8, −0.6
ΔE [cm^{-1}]	435	454	589
parameter	**m-1/4w-16**	**m-1/4w-17**	**m-1/4w-18**
			
A, B, C [MHz]	778, 321, 295	693, 331, 283	593, 392, 303
μ_a, μ_b, μ_c [D]	0.4, −0.8, −0.1	0.3, 0.7, −1.2	−2.3, −1.1, 1.6
ΔE [cm^{-1}]	599	651	771

[a] calculated at the MP2/aug-cc-PVTZ level on the top of the B3LYP-D3(BJ)/def2-TZVP geometry.

Table S7: B3LYP-D3(BJ)/def2-TZVP calculated low energy isomers of the 1,7DSU···$(H_2O)_5$ cluster and their spectroscopic parameters..

parameter	**m-1/5w-1**	**m-1/5w-2**	**m-1/5w-3**
			
A, *B*, *C* [MHz]	489, 369, 287	518, 345, 279	510, 351, 278
μ_a, μ_b, μ_c [D]	0.5, 1.4, 0.6	0.1, −1.4, −0.8	−0.2, 1.7, −0.8
ΔE [cm^{-1}][a]	0	28	33
parameter	**m-1/5w-4**	**m-1/5w-5**	**m-1/5w-6**
			
A, *B*, *C* [MHz]	491, 366, 287	486, 373, 288	488, 370, 287
μ_a, μ_b, μ_c [D]	−0.8, −1.4, 1.0	0.9, −0.3, 0.7	−0.8, 0.0, −0.8
ΔE [cm^{-1}]	38	43	49
parameter	**m-1/5w-7**	**m-1/5w-8**	**m-1/5w-9**
			
A, *B*, *C* [MHz]	541, 327, 274	519, 343, 279	530, 342, 284
μ_a, μ_b, μ_c [D]	−2.0, −1.4, −1.2	0.3, 1.4, 1.3	−1.6, −1.7, -0.9
ΔE [cm^{-1}]	53	63	90
parameter	**m-1/5w-10**	**m-1/5w-11**	**m-1/5w-12**

			
A, B, C [MHz]	514, 348, 278	489, 364, 283	545, 337, 263
μ_a, μ_b, μ_c [D]	0.0, −1.1, −1.0	−0.6, 0.9, −0.7	1.6, 0.6, −1.9
ΔE [cm^{-1}]	106	141	147
parameter	**m-1/5w-13**	**m-1/5w-14**	**m-1/5w-15**
			
A, B, C [MHz]	498, 363, 285	547, 316, 269	536, 334, 281
μ_a, μ_b, μ_c [D]	1.0, −0.6, 0.3	−2.0, −1.6, −1.0	−1.7, −1.7, −0.7
ΔE [cm^{-1}]	162	344	355
parameter	**m-1/5w-16**	**m-1/5w-17**	**m-1/5w-18**
			
A, B, C [MHz]	528, 342, 263	485, 349, 276	485, 347, 275
μ_a, μ_b, μ_c [D]	−1.7, −0.3, −2.1	1.1, 0.8, 1.1	0.9, −1.0, −0.8
ΔE [cm^{-1}]	410	502	560

[a] calculated at the MP2/aug-cc-PVTZ level on the top of the B3LYP-D3(BJ)/def2-TZVP geometry.

Table S8. The result of NBO analysis for the 1,7DSU···H_2O cluster.

1W-1					
From $C_9H_{16}O_2$ to H_2O			**From H_2O to $C_9H_{16}O_2$**		
Donor NBO[a]	Acceptor NBO[b]	$E^{(2)}$/kcal/mol	Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol
BD(1)C6-O7	BD*(1)O28-H29	0.08	BD(1)O28-H29	RY*(5)C6	0.07
BD(1)C6-O2	BD*(1)O28-H29	0.06	BD(1)O28-H29	RY*(2)O2	0.19
BD(1)C5-H21	BD*(1)O28-H30	0.05	BD(1)O28-H29	RY*(7)O2	0.07
BD(1)C3-H25	BD*(1)O28-H30	0.06	BD(1)O28-H29	BD*(1)C11-H12	0.05
LP(1)O2	RY*(1)H29	0.10	BD(1)O28-H29	BD*(1)C6-O7	0.12
LP(1)O2	BD*(1)O28-H29	**2.12**	BD(1)O28-H29	BD*(1)C6-O2	0.11
LP(1)O2	RY*(1)O28	0.08	BD(1)O28-H29	BD*(1)C1-O2	0.10
LP(1)O2	RY*(1)H29	0.10	BD(1)O28-H30	RY*(1)H25	0.09
LP(1)O2	RY*(4)H29	0.19	BD(1)O28-H30	RY*(2)H25	0.05
LP(1)O2	BD*(1)O28-H29	**6.51**	BD(1)O28-H30	RY*(1)H21	0.12
			LP(1)O28	BD*(1)C3-H25	0.07
			LP(1)O28	BD*(1)C11-H12	0.37
			LP(1)O28	BD*(1)C3-H25	0.09

[a] BD for 2-center bond, LP for 1-center valence lone pair the unstarred and starred labels corresponding to Lewis and non-Lewis NBOs, respectively.

[b] RY* for 1-center Rydberg, and BD* for 2-center antibond, the unstarred and starred labels corresponding to Lewis and non-Lewis NBOs, respectively.

Table S9. The result of NBO analysis for the most stable isomer of the 1,7DSU···$(H_2O)_2$ cluster.

2w-1					
From $C_9H_{16}O_2$ to H_2O[a]			**From $C_9H_{16}O_2$ to H_2O[b]**		
Donor NBO[c]	Acceptor NBO[d]	$E^{(2)}$/kcal/mol	Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol
BD(1)O7-C6	BD*(1)O28-H29	0.07	BD(1)C3-H25	BD*(1)O31-H33	0.13
BD(1)C11-H12	BD*(1)O28-H30	0.09			
LP(1)O2	RY*(2)H29	0.05			
LP(1)O2	RY*(3)H29	0.23			
LP(1)O2	BD*(1)O28-H29	**4.63**			
LP(2)O2	RY*(1)O28	0.08			
LP(2)O2	RY*(1)H29	0.05			
LP(2)O2	RY*(2)H29	0.10			
LP(2)O2	RY*(4)H29	0.07			
LP(2)O2	RY*(7)H29	0.09			
LP(2)O2	BD*(1)O28-H29	**8.88**			
From H_2O[a] to $C_9H_{16}O_2$			**From H_2O[a] to H_2O[b]**		
Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol	Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol
BD(1)O28-H30	RY*(8)O2	0.09	BD(1)O28-H30	RY*(5)H32	0.13
BD(1)O28-H30	RY*(1)H12	0.36	BD(1)O28-H29	BD*(1)O31-H32	0.12
BD(1)O28-H30	RY*(3)H12	0.07	LP(1)O28	BD*(1)O31-H32	0.14
BD(1)O28-H29	RY*(1)O2	0.05	LP(2)O28	RY*(4)H32	0.24
BD(1)O28-H29	RY*(2)O2	0.30	LP(2)O28	BD*(1)O31-H32	**11.26**
BD(1)O28-H29	RY*(6)O2	0.08			
BD(1)O28-H29	BD*(1)O7-C6	0.05			
BD(1)O28-H29	BD*(1)C6-O2	0.17			
BD(1)O28-H29	BD*(1)C1-O2	0.15			
LP(1)O28	BD*(1)C6-O2	0.06			
LP(1)O28	BD*(1)C11-H12	0.14			
From H_2O[b] to $C_9H_{16}O_2$			**From H_2O[b] to H_2O[a]**		
Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol	Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol
BD(1)O31-H33	RY*(4)H21	0.14	BD(1)O31-H32	BD*(1)O28-H30	0.13
BD(1)O31-H33	RY*(1)H25	0.53			
BD(1)O31-H32	RY*(1)H21	0.05			
BD(1)O31-H32	RY*(2)H21	0.16			
BD(1)O31-H32	RY*(3)H21	0.07			
LP(1)O31	RY*(2)H25	0.07			
LP(1)O31	BD*(1)C5-H21	0.06			
LP(1)O31	BD*(1)C3-H25	0.45			
LP(2)O31	RY*(1)H21	0.47			
LP(2)O31	BD*(1)C5-H20	0.06			
LP(2)O31	BD*(1)C5-H21	**1.32**			

[a] The oxygen atom number 28 of water. [b] The oxygen atom number 31 of water. [c] BD for 2-center bond, LP for 1-center valence lone pair the unstarred and starred labels corresponding to Lewis and non-Lewis NBOs, respectively. [d] RY* for 1-center Rydberg, and BD* for 2-center antibond, the unstarred and starred labels corresponding to Lewis and non-Lewis NBOs, respectively.

Table S10. The result of NBO analysis for the most stable isomer of the 1,7DSU···$(H_2O)_3$ cluster.

3w-1					
From $C_9H_{16}O_2$ to H_2O^b			**From $C_9H_{16}O_2$ to H_2O^c**		
Donor NBO[d]	Acceptor NBO[e]	$E^{(2)}$/kcal/mol	Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol
BD(1)C5-H21	BD*(1)O31-H33	0.08	BD(1)C11-H12	BD*(1)O34-H36	0.11
From $C_9H_{16}O_2$ to H_2O^a			**From H_2O^b to $C_9H_{16}O_2$**		
Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol	Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol
BD(1)C6-O7	BD*(1)O28-H29	0.07	BD(1)O31-H32	RY*(1)H21	0.11
LP(1)O2	RY*(1)H29	0.06	BD(1)O31-H32	RY*(3)H21	0.10
LP(1)O2	RY*(3)H29	0.12	BD(1)O31-H32	BD*(1)C3-H25	0.06
LP(1)O2	RY*(5)H29	0.05	BD(1)O31-H33	RY*(1)H21	0.27
LP(1)O2	BD*(1)O28-H29	**3.66**	BD(1)O31-H33	RY*(2)H21	0.08
LP(2)O2	RY*(1)O28	0.08	LP(1)O31	RY*(1)H21	0.47
LP(2)O2	RY*(3)H29	0.11	LP(1)O31	RY*(2)H21	0.10
LP(2)O2	RY*(5)H29	0.19	LP(1)O31	RY*(4)H21	0.06
LP(2)O2	RY*(7)H29	0.07	LP(1)O31	BD*(1)C3-H25	0.06
LP(2)O2	BD*(1)O28-H29	**6.82**	LP(1)O31	BD*(1)C5-H21	0.62
			LP(2)O31	BD*(1)C3-H25	0.11
From H_2O^b to H_2O^c			**From H_2O^b to H_2O^a**		
Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol	Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol
BD(1)O31-H32	RY*(1)H35	0.06	BD(1)O31-H33	RY*(2)O28	0.07
BD(1)O31-H32	RY*(5)H35	0.12			
BD(1)O31-H32	BD*(1)O34-H35	0.22			
BD(1)O31-H33	RY*(5)H35	0.09			
LP(1)O31	RY*(2)H35	0.06			
LP(1)O31	BD*(1)O34-H35	0.17			
LP(2)O31	RY*(4)H35	0.19			
LP(2)O31	RY*(6)H35	0.07			
LP(2)O31	BD*(1)O34-H35	**8.58**			
From H_2O^c to $C_9H_{16}O_2$			**From H_2O^c to H_2O^b**		
Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol	Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol
BD(1)O34-H36	RY*(1)H12	0.32	BD(1)O11-H35	BD*(1)O31-H33	0.18
BD(1)O34-H36	RY*(3)H12	0.10			
BD(1)O34-H35	RY*(1)H12	0.08			
BD(1)O34-H35	RY*(2)H12	0.24			
LP(1)O34	RY*(1)H12	0.67			
LP(1)O34	RY*(2)H12	0.06			
LP(1)O34	RY*(3)H12	0.15			
LP(1)O34	BD*(1)C11-H12	0.95			
LP(2)O34	RY*(1)H12	0.07			
LP(2)O34	BD*(1)C11-H12	0.11			
From H_2O^c to H_2O^a			**From H_2O^a to $C_9H_{16}O_2$**		
Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol	Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol
BD(1)O34-H36	RY*(2)H30	0.07	BD(1)O28-H29	RY*(2)O2	**0.22**

BD(1)O34-H36	BD*(1)O28-H30	0.08	BD(1)O28-H29	RY*(7)O2	0.06
BD(1)O34-H35	RY*(5)H30	0.10	BD(1)O28-H29	BD*(1)C1-O2	0.13
LP(2)O34	RY*(4)H30	0.13	BD(1)O28-H29	BD*(1)O2-C6	0.16
LP(2)O34	BD*(1)O28-H30	**4.45**	LP(1)O28	BD*(1)C11-H12	0.05
			LP(2)O28	RY*(2)O2	0.05
From H_2O^a to H_2O^b			**From H_2O^a to H_2O^c**		
Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol	Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol
BD(1)O28-H30	RY*(1)H32	0.06	BD(1)O28-H30	BD*(1)O34-H36	0.22
BD(1)O28-H30	RY*(5)H32	0.10			
BD(1)O28-H30	RY*(6)H32	0.09			
BD(1)O28-H30	BD*(1)O31-H32	0.37			
BD(1)O28-H29	RY*(5)H32	0.07			
BD(1)O28-H29	BD*(1)O31-H32	0.11			
CR(1)O28	BD*(1)O31-H32	0.05			
LP(1)O28	RY*(1)H32	0.07			
LP(1)O28	BD*(1)O31-H32	0.32			
LP(2)O28	RY*(4)H32	0.21			
LP(2)O28	BD*(1)O31-H32	**17.32**			
LP(2)O28	BD*(1)O31-H33	0.05			

[a] The oxygen atom number 28 of water.

[b] The oxygen atom number 31 of water.

[c] The oxygen atom number 34 of water.

[d] BD for 2-center bond, LP for 1-center valence lone pair the unstarred and starred labels corresponding to Lewis and non-Lewis NBOs, respectively.

[e] RY* for 1-center Rydberg, and BD* for 2-center antibond, the unstarred and starred labels corresponding to Lewis and non-Lewis NBOs, respectively.

Table S11. The result of NBO analysis for the most stable isomer of the 1,7DSU···$(H_2O)_4$ cluster.

4w-1

From $C_9H_{16}O_2$ to H_2O[b]			**From $C_9H_{16}O_2$ to H_2O[c]**		
Donor NBO[e]	Acceptor NBO[f]	$E^{(2)}$/kcal/mol	Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol
BD(1)C1-H27	BD*(1)O31-H32	0.10	BD(1)O7-C6	BD*(1)O34-H35	0.09
			BD(1)C6-O2	BD*(1)O34-H35	0.07
			LP(1)O2	BD*(1)O34-H35	**1.64**
			LP(2)O2	RY*(5)H35	0.10
			LP(2)O2	RY*(7)H35	0.06
			LP(2)O2	BD*(1)O34-H35	**4.32**
From $C_9H_{16}O_2$ to H_2O[a]			**From H_2O[b] to $C_9H_{16}O_2$**		
Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol	Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol
BD(1)C6-C5	BD*(1)O28-H29	0.10	BD(1)O31-H32	RY*(2)C1	0.05
BD(1)C10-H14	BD*(1)O28-H30	0.10	BD(1)O31-H32	RY*(1)H27	0.17
BD(1)C10-H14	BD*(1)O28-H29	0.08	BD(1)O31-H32	RY*(3)H27	0.06
LP(1)O2	RY*(4)H29	0.08	BD(1)O31-H33	RY*(4)H27	0.11
LP(1)O2	BD*(1)O28-H29	**4.20**	BD(1)O31-H33	RY*(2)O2	0.07
LP(2)O2	BD*(1)O28-H29	0.71	LP(1)O31	RY*(1)H27	0.18
			LP(1)O31	BD*(1)C1-H27	0.63
From H_2O[b] to H_2O[c]			**From H_2O[b] to H_2O[a]**		
Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol	Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol
BD(1)O31-H32	RY*(2)O34	0.07	BD(1)O31-H32	RY*(1)H30	0.07
BD(1)O31-H33	RY*(5)H35	0.05	BD(1)O31-H32	RY*(5)H30	0.06
			BD(1)O31-H33	RY*(5)H30	0.09
			BD(1)O31-H33	BD*(1)O28-H30	0.13
			LP(1)O31	RY*(1)H30	0.05
			LP(1)O31	BD*(1)O28-H30	0.11
			LP(2)O31	RY*(1)O28	0.10
			LP(2)O31	RY*(4)H30	0.22
			LP(2)O31	RY*(5)H30	0.05
			LP(2)O31	BD*(1)O28-H30	**9.41**
From H_2O[c] to $C_9H_{16}O_2$			**From H_2O[c] to H_2O[b]**		
Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol	Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol
BD(1)O34-H35	RY*(2)O2	0.50	BD(1)O34-H36	RY*(5)H33	0.10
BD(1)O34-H35	BD*(1)O7-C6	0.06	BD(1)O34-H36	BD*(1)O31-H33	0.12
BD(1)O34-H35	BD*(1)C6-O2	0.08	BD(1)O34-H35	RY*(5)H33	0.06
BD(1)O34-H35	BD*(1)C1-O2	0.07	BD(1)O34-H35	BD*(1)O31-H33	0.26
LP(1)O34	BD*(1)C6-O2	0.06	LP(1)O34	RY*(1)H33	0.14
LP(2)O34	RY*(1)H12	0.06	LP(1)O34	BD*(1)O31-H33	0.31
LP(2)O34	BD*(1)C11-H12	0.09	LP(2)O34	RY*(1)O31	0.07
			LP(2)O34	RY*(4)H33	0.20
			LP(2)O34	RY*(6)H33	0.10
			LP(2)O34	BD*(1)O31-H32	0.06
			LP(2)O34	BD*(1)O31-H33	**17.14**

From H_2O^c to H_2O^d			From H_2O^a to $C_9H_{16}O_2$		
Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol	Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol
BD(1)O34-H36	BD*(1)O37-H38	0.24	BD(1)O28-H30	RY*(1)H14	0.32
			BD(1)O28-H29	RY*(1)O2	0.24
			BD(1)O28-H29	RY*(2)O2	0.24
			BD(1)O28-H29	RY*(13)O2	0.06
			BD(1)O28-H29	RY*(1)H14	0.20
			BD(1)O28-H29	BD*(1)C6-O2	0.14
			BD(1)O28-H29	BD*(1)C6-O2	0.07
			BD(1)O28-H29	BD*(1)C10-H14	0.18
			LP(1)O28	RY*(3)O2	0.06
			LP(1)O28	BD*(1)C6-O2	0.12
			LP(1)O28	BD*(1)C10-H14	0.10
			LP(2)O28	BD*(1)C10-H14	0.13
From H_2O^a to H_2O^b			From H_2O^a to H_2O^d		
Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol	Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol
BD(1)O28-H30	BD*(1)O31-H32	0.24	BD(1)O28-H30	RY*(5)H39	0.08
			BD(1)O28-H30	BD*(1)O37-H39	0.14
			BD(1)O28-H29	RY*(5)H39	0.07
			BD(1)O28-H29	BD*(1)O37-H39	0.18
			LP(1)O28	RY*(1)H39	0.15
			LP(1)O28	BD*(1)O37-H39	0.26
			LP(2)O28	RY*(1)O37	0.05
			LP(2)O28	RY*(4)H39	0.19
			LP(2)O28	RY*(6)H39	0.10
			LP(2)O28	BD*(1)O37-H39	**16.82**
			LP(2)O28	BD*(1)O37-H38	0.05
From H_2O^d to $C_9H_{16}O_2$			From H_2O^d to H_2O^c		
Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol	Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol
BD(1)O37-H39	RY*(2)O2	0.09	BD(1)O37-H39	RY*(5)H36	0.09
BD(1)O37-H39	RY*(2)H14	0.09	BD(1)O37-H39	BD*(1)O34-H36	0.17
BD(1)O37-H38	RY*(1)H12	0.11	BD(1)O37-H38	RY*(1)H36	0.08
LP(1)O37	RY*(2)H12	0.11	BD(1)O37-H38	RY*(5)H36	0.06
LP(1)O37	BD*(1)C11-H12	0.14	LP(1)O37	RY*(1)H36	0.07
			LP(1)O37	BD*(1)O34-H36	0.14
			LP(2)O37	RY*(1)O34	0.12
			LP(2)O37	RY*(4)H36	0.23
			LP(2)O37	BD*(1)O34-H36	**10.12**

[a] The oxygen atom number 28 of water. [b] The oxygen atom number 31 of water. [c] The oxygen atom number 34 of water. [d] The oxygen atom number 37 of water. [e] BD for 2-center bond, LP for 1-center valence lone pair the unstarred and starred labels corresponding to Lewis and non-Lewis NBOs, respectively. [f] RY* for 1-center Rydberg, and BD* for 2-center antibond, the unstarred and starred labels corresponding to Lewis and non-Lewis NBOs, respectively.

Table S12. The result of NBO analysis for the most stable isomer of the 1,7DSU···$(H_2O)_5$ cluster.

5w-1					
From $C_9H_{16}O_2$ to H_2O^c			**From $C_9H_{16}O_2$ to H_2O^b**		
Donor NBO[f]	Acceptor NBO[g]	$E^{(2)}$/kcal/mol	Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol
BD(1)O2-C6	BD*(1)O34-H35	0.06	BD(1)C1-H27	BD*(1)O31-H32	0.09
BD(1)C6-O7	BD*(1)O34-H35	0.09			
LP(1)O2	RY*(1)H35	0.13			
LP(1)O2	BD*(1)O34-H35	**2.24**			
LP(2)O2	RY*(5)H35	0.11			
LP(2)O2	RY*(7)H35	0.08			
LP(2)O2	BD*(1)O34-H35	**4.92**			
From $C_9H_{16}O_2$ to H_2O^a			**From $C_9H_{16}O_2$ to H_2O^d**		
Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol	Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol
BD(1)C6-C5	BD*(1)O28-H29	0.10	BD(1)C11-H12	BD*(1)O37-H38	0.06
BD(1)C10-H14	BD*(1)O28-H30	0.05			
BD(1)C10-H14	BD*(1)O28-H29	0.08			
LP(1)O2	RY*(4)H29	0.06			
LP(1)O2	BD*(1)O28-H29	**4.38**			
LP(2)O2	RY*(4)H29	0.05			
LP(2)O2	BD*(1)O28-H29	0.85			
From H_2O^c to $C_9H_{16}O_2$			**From H_2O^c to H_2O^b**		
Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol	Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol
BD(1)O34-H35	RY*(1)O2	0.30	BD(1)O34-H36	RY*(5)H33	0.10
BD(1)O34-H35	RY*(2)O2	0.22	BD(1)O34-H35	RY*(5)H33	0.06
BD(1)O34-H35	BD*(1)C1-O2	0.09	BD(1)O34-H35	BD*(1)O31-H33	0.33
BD(1)O34-H35	BD*(1)O2-C6	0.10	CR(1)O34	BD*(1)O31-H33	0.07
BD(1)O34-H35	BD*(1)C6-O7	0.06	LP(1)O34	RY*(1)H33	0.14
LP(1)O34	BD*(1)C3-H25	0.06	LP(1)O34	BD*(1)O31-H33	0.36
LP(1)O34	BD*(1)O2-C6	0.05	LP(2)O34	RY*(1)O31	0.06
LP(2)O34	BD*(1)C11-H12	0.07	LP(2)O34	RY*(4)H33	0.28
			LP(2)O34	RY*(6)H33	0.08
			LP(2)O34	BD*(1)O31-H32	0.05
			LP(2)O34	BD*(1)O31-H33	**18.83**
From H_2O^c to H_2O^d			**From H_2O^b to $C_9H_{16}O_2$**		
Donor NBO	Donor NBO	Donor NBO	Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol
BD(1)O34-H36	BD*(1)O37-H38	0.10	BD(1)O31-H32	RY*(2)C1	0.06
			BD(1)O31-H32	RY*(1)H27	0.23
			LP(1)O31	BD*(1)C1-H27	0.35
From H_2O^b to H_2O^c			**From H_2O^b to H_2O^a**		
Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol	Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol
BD(1)O31-H32	RY*(2)O34	0.08	BD(1)O31-H32	RY*(5)H30	0.07
BD(1)O31-H33	RY*(3)H35	0.06	BD(1)O31-H33	RY*(5)H30	0.11
BD(1)O31-H33	BD*(1)O34-H36	0.06	BD(1)O31-H33	BD*(1)O28-H30	0.22
			LP(1)O31	RY*(1)H30	0.07

			LP(1)O31	BD*(1)O28-H30	0.15
			LP(2)O31	RY*(3)O28	0.10
			LP(2)O31	RY*(4)H30	0.24
			LP(2)O31	RY*(5)H30	0.08
			LP(2)O31	BD*(1)O28-H30	**13.08**
From H_2O^a to $C_9H_{16}O_2$			**From H_2O^a to H_2O^b**		
Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol	Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol
BD(1)O28-H30	RY*(2)O2	0.07	BD(1)O28-H30	BD*(1)O31-H32	0.19
BD(1)O28-H30	RY*(1)H14	0.07			
BD(1)O28-H30	RY*(2)H14	0.07			
BD(1)O28-H29	RY*(2)O2	0.43			
BD(1)O28-H29	RY*(6)O2	0.12			
BD(1)O28-H29	RY*(1)H14	0.07			
BD(1)O28-H29	RY*(2)H14	0.06			
BD(1)O28-H29	RY*(3)H14	0.05			
BD(1)O28-H29	BD*(1)C1-O2	0.08			
BD(1)O28-H29	BD*(1)O2-C6	0.14			
BD(1)O28-H29	BD*(1)C10-H14	0.18			
LP(1)O28	RY*(2)O2	0.13			
LP(1)O28	BD*(1)O2-C6	0.09			
LP(2)O28	BD*(1)C3-C1	0.06			
LP(2)O28	BD*(1)O2-C6	0.07			
LP(2)O28	BD*(1)C10-H14	0.16			
From H_2O^a to H_2O^e			**From H_2O^e to $C_9H_{16}O_2$**		
Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol	Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol
BD(1)O28-H30	RY*(5)H42	0.12	BD(1)O40-H42	RY*(1)H14	0.23
BD(1)O28-H30	BD*(1)O40-H42	0.27	BD(1)O40-H42	BD*(1)C10-H14	0.08
BD(1)O28-H29	BD*(1)O10-H42	0.13	BD(1)O40-H41	RY*(1)H14	0.15
CR(1)O28	BD*(1)O40-H42	0.12	BD(1)O40-H41	RY*(2)H14	0.07
LP(1)O28	RY*(1)H42	0.11	LP(1)O40	RY*(1)H14	0.21
LP(1)O28	BD*(1)O40-H42	0.42	LP(1)O40	BD*(1)C10-H14	0.14
LP(2)O28	RY*(1)O40	0.07	LP(2)O40	RY*(1)H14	0.08
LP(2)O28	RY*(4)H42	0.34			
LP(2)O28	RY*(8)H42	0.10			
LP(2)O28	BD*(1)O40-H42	**22.35**			
From H_2O^e to H_2O^a			**From H_2O^e to H_2O^d**		
Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol	Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol
BD(1)O40-H41	RY*(2)O28	0.09	BD(1)O40-H42	RY*(5)H39	0.12
			BD(1)O40-H42	BD*(1)O37-H39	0.20
			BD(1)O40-H41	RY*(1)H39	0.08
			BD(1)O40-H41	RY*(5)H39	0.12
			CR(1)O40	BD*(1)O37-H39	0.08
			LP(1)O40	BD*(1)O37-H39	0.32
			LP(2)O40	RY*(1)O37	0.14

			LP(2)O40	RY*(4)H39	0.32
			LP(2)O40	RY*(6)H39	0.17
			LP(2)O40	BD*(1)O37-H39	**18.62**
From H_2O^d to $C_9H_{16}O_2$			**From H_2O^d to H_2O^c**		
Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol	Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol
BD(1)O37-H38	RY*(1)H12	0.24	BD(1)O37-H33	RY*(5)H36	0.09
BD(1)O37-H39	RY*(2)H12	0.07	BD(1)O37-H34	RY*(5)H36	0.11
LP(1)O37	RY*(1)H12	0.38	BD(1)O37-H34	BD*(1)O34-H36	0.11
LP(1)O37	RY*(2)H12	0.08	LP(1)O37	RY*(1)H36	0.08
LP(1)O37	BD*(1)C11-H12	0.42	LP(1)O37	BD*(1)O34-H36	0.16
LP(2)O37	RY*(1)H12	0.07	LP(2)O37	RY*(1)O34	0.19
LP(2)O37	BD*(1)C11-H12	0.07	LP(2)O37	RY*(4)H36	0.26
			LP(2)O37	RY*(5)H36	0.09
			LP(2)O37	BD*(1)O34-H36	**14.25**
From H_2O^d to H_2O^e					
Donor NBO	Acceptor NBO	$E^{(2)}$/kcal/mol			
BD(1)O37-H39	BD*(1)O40-H41	0.15			
LP(2)O37	RY*(1)O40	0.06			

[a] The oxygen atom number 28 of water. [b] The oxygen atom number 31 of water. [c] The oxygen atom number 34 of water. [d] The oxygen atom number 37 of water. [e] The oxygen atom number 40 of water. [f] BD for 2-center bond, LP for 1-center valence lone pair the unstarred and starred labels corresponding to Lewis and non-Lewis NBOs, respectively. [g] RY* for 1-center Rydberg, and BD* for 2-center antibond, the unstarred and starred labels corresponding to Lewis and non-Lewis NBOs, respectively.

Table S13. Measured transition lines for 1,7DSU: Residual between observed frequency and that calculated (SPFIT) from the spectroscopic parameters (MHz), with the experimental accuracy of 0.005 MHz for all lines.

J'	Ka′	Kc′	J''	Ka''	Kc′′	ν_{obs}/MHz	$\Delta\nu_{obs-calc}$/kHz
2	2	0	1	1	1	7490.1054	0.4
2	2	1	1	1	0	7457.6789	0.3
3	3	0	2	2	1	11906.4332	-0.3
3	3	1	2	2	0	11905.8787	-1.1
4	1	4	3	0	3	7832.4768	-5.6
4	2	3	3	1	2	10677.5050	-3.2
4	3	1	3	2	2	13557.3497	0.7
4	3	2	3	2	1	13554.5680	-2.2
4	4	0	3	3	1	16338.6309	-5.2
4	4	0	4	3	1	9738.2933	-4.0
4	4	1	3	3	0	16338.6309	0.7
4	4	1	4	3	2	9738.3248	-13.6
5	0	5	4	1	4	6999.3882	6.4
5	1	5	4	0	4	9405.7119	-5.6
5	2	4	4	1	3	12263.4446	-1.8
5	3	2	4	2	3	15209.5219	2.4
5	3	3	4	2	2	15201.1520	2.6
5	4	1	5	3	2	9737.5648	-4.9
5	4	2	5	3	3	9737.7331	-0.7
6	0	6	5	1	5	8712.2159	1.8
6	1	6	5	0	5	10966.5615	-2.3
6	2	5	5	1	4	13833.5399	0.2
6	3	3	5	2	4	16863.7140	3.0
6	3	4	5	2	3	16844.1094	3.4
6	4	2	6	3	3	9736.2536	-0.6
6	4	3	6	3	4	9736.7466	1.1
6	5	1	6	4	2	12520.3529	-2.8
6	5	2	6	4	3	12520.3529	-5.1
7	0	7	6	1	6	10431.7009	-2.7
7	1	7	6	0	6	12516.9531	4.4
7	4	3	7	3	4	9734.0597	3.5
7	4	4	7	3	5	9735.2853	4.6
7	5	2	7	4	3	12519.5675	-1.7
7	5	3	7	4	4	12519.5774	-0.5
8	0	8	7	1	7	12155.1784	0.2
8	1	8	7	0	7	14059.1465	2.0
8	4	4	8	3	5	9730.5936	5.8
8	4	5	8	3	6	9733.2790	7.8
8	5	3	8	4	4	12518.3983	7.3
8	5	4	8	4	5	12518.4159	-0.9
9	0	9	8	1	8	13879.8655	-3.6

Table S14. Measured transition lines for 1,7DSU···H_2O: Residual between observed frequency and that calculated (SPFIT) from the spectroscopic parameters (MHz), with the experimental accuracy of 0.005 MHz for all lines.

J'	Ka'	Kc'	J''	Ka''	Kc''	ν_{obs}/MHz	$\Delta\nu_{obs-calc}$/kHz
4	4	0	3	3	1	9260.5862	-1.8
4	4	0	3	3	0	9256.4625	-0.2
4	4	1	3	3	0	9256.0113	-0.8
4	4	1	3	3	1	9260.1372	-0.2
5	0	5	4	0	4	6403.162	-0.9
5	0	5	4	1	4	6283.8827	3.0
5	1	4	4	1	3	7019.7546	2.2
5	1	5	4	1	4	6342.1473	-0.2
5	1	5	4	0	4	6461.4304	-0.3
5	2	3	4	2	2	7166.9457	-0.6
5	2	4	4	2	3	6752.2922	0.9
5	3	2	4	3	1	6971.2903	0.1
5	3	3	4	3	2	6892.6047	0.8
5	4	1	4	3	2	10645.5087	-1.9
5	4	1	4	3	1	10617.3631	-0.5
5	4	2	4	3	1	10613.3756	-0.1
5	4	2	4	3	2	10641.5219	-0.7
5	5	0	4	4	0	11707.0385	2.2
5	5	1	4	4	1	11707.4414	-1.1
6	0	6	5	0	5	7602.1002	-0.2
6	0	6	5	1	5	7543.833	0.5
6	1	5	5	1	4	8292.4363	0.5
6	1	5	5	2	4	7615.7511	-0.3
6	1	6	5	1	5	7570.267	-2.9
6	1	6	5	0	5	7628.5388	1.1
6	2	4	5	2	3	8617.3463	-0.2
6	2	5	5	2	4	8049.226	0.4
6	3	3	5	3	2	8452.7426	-1.1
6	3	3	5	2	3	10688.7088	2.4
6	3	4	5	3	3	8267.7679	-0.3
6	4	2	5	4	1	8302.3611	-1.0
6	4	2	5	3	2	11948.437	1.4
6	4	3	5	4	2	8286.9931	-0.6
6	4	3	5	3	3	12035.911	-1.5
6	5	1	5	4	2	13082.4772	3.0
6	5	1	5	4	1	13078.4855	-0.7
6	5	2	5	4	1	13078.0023	-1.4
6	5	2	5	4	2	13081.991	-0.7
6	6	0	5	5	1	14155.8845	-2.1
6	6	0	5	5	0	14155.8439	1.8
6	6	1	5	5	0	14155.8439	5.9

6	6	1	5	5	1	14155.8845	2.0
7	0	7	6	0	6	8806.0604	0.3
7	0	7	6	1	6	8779.6228	0.1
7	1	6	6	1	5	9508.1601	0.4
7	1	7	6	1	6	8791.0356	-1.4
7	1	7	6	0	6	8817.4754	1.1
7	2	5	6	2	4	10018.643	-0.1
7	2	6	6	2	5	9323.1211	-0.6
7	3	4	6	3	3	9966.2191	0.2
7	3	4	6	2	4	12037.5773	-1.5
7	3	5	6	3	4	9626.885	1.4
7	4	3	6	4	2	9735.6385	-0.4
7	4	3	6	3	3	13231.3331	2.3
7	4	4	6	4	3	9687.4562	1.6
7	4	4	6	3	4	13455.5993	0.5
7	5	2	6	5	1	9664.3072	2.4
7	5	2	6	4	2	14440.4276	-1.3
7	5	3	6	5	2	9661.9533	0.7
7	5	3	6	4	3	14456.9477	-2.8
7	6	1	6	5	1	15529.3898	-1.6
7	6	2	6	5	2	15529.8189	-2.1
7	7	0	6	6	1	16604.2233	-1.2
7	7	0	6	6	0	16604.2233	2.9
7	7	1	6	6	0	16604.2233	3.2
7	7	1	6	6	1	16604.2233	-0.9
8	0	8	7	0	7	10014.3178	-0.7
8	1	7	7	1	6	10695.1287	1.0
8	1	7	7	2	6	10446.6919	0.4
8	1	8	7	1	7	10007.6627	0.2
8	2	6	7	2	5	11356.2294	-0.6
8	2	7	7	2	6	10576.4441	-0.5
8	2	7	7	1	6	10824.8773	-3.5
8	3	5	7	3	4	11477.369	0.8
8	3	5	7	2	5	13496.3036	-0.3
8	3	6	7	3	5	10963.8725	0.2
8	4	4	7	4	3	11205.7364	-1.4
8	4	5	7	4	4	11086.1379	-0.4
8	5	3	7	5	2	11075.6214	0.5
8	5	3	7	4	3	15780.4105	-0.4
8	5	4	7	5	3	11066.5582	-2.0
8	5	4	7	4	4	15836.0586	2.5
8	6	2	7	5	2	16899.4822	-0.2
8	6	3	7	5	3	16901.9505	-2.7
8	8	0	7	7	0	19052.3051	-1.4

8	8	1	7	7	1	19052.3051	-1.8
9	0	9	8	0	8	11225.0227	0.6
9	1	8	8	1	7	11880.1655	0.9
9	1	9	8	1	8	11222.1956	-0.9
9	2	7	8	2	6	12621.7225	1.0
9	2	8	8	2	7	11813.6455	-0.6
9	3	6	8	3	5	12950.6758	1.3
9	3	7	8	3	6	12275.2589	-0.5
9	4	5	8	4	4	12719.1403	-2.2
9	4	6	8	4	5	12475.4603	-1.8
9	5	4	8	5	3	12505.3194	1.4
9	5	4	8	4	4	17079.992	0.9
9	5	5	8	5	4	12477.5129	0.7
9	5	5	8	4	5	17227.4302	0.2
9	6	3	8	5	3	18261.742	-0.1
9	6	4	8	5	4	18271.8615	0.4
10	0	10	9	0	9	12436.9243	0.2
10	1	9	9	1	8	13073.6771	0.7
10	1	9	9	2	8	13010.4394	-2.4
10	1	10	9	1	9	12435.7583	-2.5
10	2	8	9	2	7	13825.3142	2.8
10	2	9	9	2	8	13039.7497	-0.5
10	3	7	9	3	6	14363.4844	-0.4
10	3	8	9	3	7	13560.6238	-0.9
10	4	6	9	4	5	14262.3409	-1.0
10	4	7	9	4	6	13847.5863	2.2
10	5	5	9	5	4	13962.7867	0.9
11	0	11	10	0	10	13649.3724	-1.0
11	1	10	10	1	9	14275.3137	2.7
11	1	11	10	1	10	13648.9072	1.7
11	2	9	10	2	8	14997.4434	-3.8
11	2	10	10	2	9	14259.0906	2.3

Table S15. Measured Transition Lines for 1,7DSU···$H_2{}^{18}O$: Residual between observed frequency and that calculated (SPFIT) from the spectroscopic parameters (MHz), with the experimental accuracy of 0.005 MHz for all lines.

J'	Ka′	Kc′	J''	Ka′′	Kc′′	ν_{obs}/MHz	$\Delta\nu_{obs-calc}$/kHz
4	4	0	3	3	1	8963.5314	-4.7
4	4	0	3	3	0	8958.3093	0.1
4	4	1	3	3	0	8957.6775	-1.7
4	4	1	3	3	1	8962.9059	-0.2
5	0	5	4	0	4	6239.7335	1.1
5	1	4	4	1	3	6879.8371	2.7
5	1	5	4	1	4	6187.473	0.2
5	2	3	4	1	3	8356.1467	0.2
5	3	2	4	2	2	9133.6157	2.4
5	3	3	4	2	3	9451.5079	0.9
5	4	1	4	3	2	10328.0911	-1.1
5	4	1	4	3	1	10292.6339	-0.2
5	4	2	4	3	1	10287.0794	0.3
5	4	2	4	3	2	10322.5376	0.4
5	5	0	4	4	0	11327.6229	-1.1
5	5	1	4	4	1	11328.1858	0.3
6	0	6	5	0	5	7407.368	0.8
6	1	5	5	1	4	8106.0915	0.2
6	1	6	5	1	5	7381.8886	0.9
6	2	4	5	1	4	9960.6091	-2.9
6	3	3	5	2	3	10411.314	1.9
6	3	4	5	2	4	10956.7296	-0.2
6	4	2	5	3	3	11725.1646	0.2
6	4	2	5	3	2	11592.1824	0.1
6	4	3	5	3	2	11565.4036	-0.3
6	4	3	5	3	3	11698.3878	1.8
6	5	1	5	4	2	12680.161	-0.4
6	5	1	5	4	1	12674.6051	-1.4
6	5	2	5	4	1	12673.8629	-1.5
6	5	2	5	4	2	12679.4185	-0.9
6	6	0	5	5	0	13694.8243	4.5
6	6	1	5	5	1	13694.8786	-2.7
7	0	7	6	0	6	8580.6549	1.4
7	0	7	6	1	6	8561.6312	2.1
7	1	6	6	1	5	9277.2871	-1.2
7	1	7	6	1	6	8569.3741	0.1
7	1	7	6	0	6	8588.3998	1.4
7	2	5	6	2	4	9843.346	1.2
7	2	5	6	1	5	11697.8632	-2.2
7	2	6	6	2	5	9116.4181	-1.0
7	3	4	6	3	3	9843.3718	-1.4

7	3	4	6	2	4	11770.3877	2.3
7	3	5	6	3	4	9449.0216	-1.6
7	3	5	6	2	5	12527.0802	-0.8
7	4	3	6	4	2	9593.0239	0.2
7	4	3	6	3	3	12840.895	2.3
7	4	4	6	4	3	9527.4739	-2.1
7	4	4	6	3	4	13104.5886	0.9
7	5	2	6	4	2	14009.5696	-0.3
7	5	3	6	4	3	14032.0089	-0.4
7	6	1	6	5	1	15044.5176	1.4
7	6	2	6	5	2	15045.1681	-0.4
7	7	0	6	6	1	16061.5092	-3.7
7	7	0	6	6	0	16061.5087	2.8
7	7	1	6	6	0	16061.5092	3.9
7	7	1	6	6	1	16061.5087	-3.6
8	0	8	7	0	7	9757.9194	2.3
8	0	8	7	1	7	9750.1726	0.4
8	1	7	7	1	6	10428.2999	-2.9
8	1	8	7	1	7	9753.2183	0.1
8	1	8	7	0	7	9760.9619	-1.2
8	2	6	7	2	5	11128.2746	-1.4
8	2	7	7	2	6	10332.9997	-2.3
8	3	5	7	3	4	11325.7428	1.4
8	3	5	7	2	5	13252.7854	3.4
8	3	6	7	3	5	10750.7778	-2.5
8	4	4	7	4	3	11059.2897	1.3
8	4	4	7	3	4	14056.8091	1.1
8	4	5	7	4	4	10900.8359	-0.4
8	4	5	7	3	5	14556.4023	1.5
8	5	3	7	4	3	15317.0384	-2.4
8	5	4	7	4	4	15391.2959	2.3
8	6	2	7	5	2	16389.8999	-0.7
8	6	3	7	5	3	16393.6256	1.4
9	0	9	8	0	8	10937.2291	1.8
9	1	8	8	1	7	11583.5186	-2.0
9	1	9	8	1	8	10935.351	2.1
9	2	7	8	2	6	12335.5864	0.6
9	2	8	8	2	7	11533.9953	-4.4
9	3	6	8	3	5	12755.6819	2.5
9	3	7	8	3	6	12023.7747	-3.6
9	4	5	8	4	4	12570.451	2.4
9	4	6	8	4	5	12260.5326	-2.3
10	0	10	9	0	9	12117.4698	0.3
10	1	9	9	1	8	12748.5726	-4.2

10	1	10	9	1	9	12116.7424	1.8
11	0	11	10	0	10	13298.1126	0.7
11	1	11	10	1	10	13297.8369	1.5

Table S16. Measured transition lines for 1,7DSU···D_2O: Residual between observed frequency and that calculated (SPFIT) from the spectroscopic parameters (MHz), with the experimental accuracy of 0.005 MHz for all lines.

J'	Ka′	Kc′	J''	Ka′′	Kc′′	ν_{obs}/MHz	$\Delta\nu_{obs-calc}$/kHz
4	4	0	3	3	1	8956.3157	7.0
4	4	0	3	3	0	8950.9869	-1.4
4	4	1	3	3	0	8950.3415	-0.4
4	4	1	3	3	1	8955.6614	-0.9
5	3	2	4	2	2	9135.6259	-2.9
5	3	3	4	2	3	9454.8053	6.2
5	4	1	4	3	1	10288.5072	-3.7
5	4	2	4	3	2	10318.8843	-2.4
5	5	0	4	4	0	11317.8033	4.6
5	5	1	4	4	1	11318.3623	-11.9
6	0	6	5	0	5	7424.624	2.6
6	1	5	5	1	4	8122.8334	-3.1
6	1	6	5	1	5	7399.656	0.6
6	2	4	5	2	3	8504.928	-0.9
6	2	5	5	2	4	7897.1567	-2.8
6	3	3	5	2	3	10418.3408	-3.9
6	4	2	5	3	2	11590.8928	-2.8
6	4	3	5	3	3	11698.5898	-0.9
6	5	1	5	4	1	12668.1415	0.1
6	5	2	5	4	1	12667.3793	5.2
6	5	2	5	4	2	12673.0736	1.8
6	6	0	5	5	0	13682.4923	5.0
6	6	1	5	5	1	13682.5533	2.4
7	0	7	6	0	6	8601.0153	0.5
7	0	7	6	1	6	8582.5337	-1.5
7	1	6	6	1	5	9296.1039	6.6
7	1	7	6	1	6	8590.0212	-0.1
7	1	7	6	0	6	8608.5023	1.4
7	2	5	6	2	4	9865.7271	1.9
7	2	6	6	2	5	9137.4546	0.0
7	5	2	6	4	2	14006.2526	0.8
7	5	3	6	4	3	14029.2168	0.0
7	7	0	6	6	1	16046.6919	-5.9
7	7	0	6	6	0	16046.6919	1.4
7	7	1	6	6	0	16046.6919	2.1
7	7	1	6	6	1	16046.6919	-5.2
8	0	8	7	0	7	9781.3508	1.6
8	0	8	7	1	7	9773.8623	-0.8
8	1	7	7	1	6	10449.9466	-0.1
8	1	8	7	1	7	9776.7912	-1.7
8	1	8	7	0	7	9784.2772	-1.8

8	2	6	7	2	5	11151.6489	-0.7
8	2	7	7	2	6	10356.5854	0.3

Table S17. Measured transition lines for 1,7DSU···HDO: Residual between observed frequency and that calculated (SPFIT) from the spectroscopic parameters (MHz), with the experimental accuracy of 0.005 MHz for all lines.

J'	Ka′	Kc′	J''	Ka′′	Kc′′	ν_{obs}/MHz	$\Delta\nu_{obs-calc}$/kHz
4	4	0	3	3	1	9178.8728	0.6
4	4	0	3	3	0	9174.4677	-0.4
4	4	1	3	3	0	9173.9718	-2.0
4	4	1	3	3	1	9178.3784	0.6
5	1	4	4	1	3	6985.7931	-2.5
5	3	2	4	2	2	9330.4206	-4.8
5	3	3	4	2	3	9632.3194	-3.0
5	4	1	4	3	1	10528.9416	1.4
5	4	2	4	3	2	10554.5735	0.3
5	5	0	4	4	0	11602.575	0.9
5	5	1	4	4	1	11603.0175	-0.9
6	0	6	5	0	5	7553.9275	0.4
6	1	5	5	1	4	8246.7148	-2.9
6	1	6	5	1	5	7523.9625	1.8
6	2	4	5	2	3	8586.0232	1.6
6	2	5	5	2	4	8007.6764	0.6
6	3	3	5	2	3	10614.4299	4.3
6	4	2	5	3	2	11852.2564	1.5
6	4	3	5	3	3	11944.6075	0.5
6	5	1	5	4	1	12968.146	0.3
6	5	2	5	4	1	12967.6055	3.5
6	5	2	5	4	2	12971.9732	-0.1
6	6	0	5	5	1	14028.8714	-6.0
6	6	0	5	5	0	14028.8287	1.4
6	6	1	5	5	0	14028.8287	6.2
6	6	1	5	5	1	14028.8714	-1.2
7	0	7	6	0	6	8750.3911	2.4
7	0	7	6	1	6	8726.2256	1.0
7	1	6	6	1	5	9450.938	-2.4
7	1	7	6	1	6	8736.492	0.6
7	1	7	6	0	6	8760.656	0.6
7	2	5	6	2	4	9976.86	1.1
7	2	6	6	2	5	9272.579	-1.1
7	5	2	6	4	2	14323.5783	0.9
7	5	3	6	4	3	14341.5641	-3.1
7	7	0	6	6	1	16454.6413	-3.0
7	7	0	6	6	0	16454.6413	1.7
7	7	1	6	6	0	16454.6413	2.2
7	7	1	6	6	1	16454.6413	-2.6
8	0	8	7	0	7	9951.0732	-0.1
8	0	8	7	1	7	9940.8051	-1.4

8	1	7	7	1	6	10628.6655	-2.9
8	1	8	7	1	7	9945.0184	-0.7
8	1	8	7	0	7	9955.2872	1.4
8	2	6	7	2	5	11301.1944	0.8
8	2	7	7	2	6	10516.7223	0.7

Table S18. Measured transition lines for 1,7DSU···DHO: Residual between observed frequency and that calculated (SPFIT) from the spectroscopic parameters (MHz), with the experimental accuracy of 0.005 MHz for all lines.

J'	Ka′	Kc′	J''	Ka′′	Kc′′	ν_{obs}/MHz	$\Delta\nu_{obs-calc}$/kHz
4	4	0	3	3	0	9026.1262	-0.9
4	4	1	3	3	1	9030.5493	-1.7
5	3	2	4	2	2	9202.0121	0.4
5	3	3	4	2	3	9516.0903	2.1
5	4	1	4	3	1	10369.9104	-3.5
5	4	2	4	3	2	10398.747	-0.5
5	5	0	4	4	0	11413.4712	3.5
5	5	1	4	4	1	11413.9999	1.0
6	0	6	5	0	5	7470.4116	1.9
6	1	5	5	1	4	8167.6746	-5.2
6	1	6	5	1	5	7443.9262	0.9
6	2	4	5	2	3	8536.4832	-2.0
6	2	5	5	2	4	7937.4626	1.5
6	3	3	5	2	3	10485.6914	1.3
6	4	2	5	3	2	11679.8013	0.8
6	4	3	5	3	3	11782.5721	0.8
6	5	1	5	4	1	12769.5234	0.3
6	5	2	5	4	2	12774.0809	-1.6
6	6	0	5	5	1	13798.8314	-6.5
6	6	0	5	5	0	13798.774	-0.3
6	6	1	5	5	0	13798.774	6.1
6	6	1	5	5	1	13798.8314	-0.1
7	0	7	6	0	6	8653.9398	2.4
7	0	7	6	1	6	8633.8004	-1.5
7	1	6	6	1	5	9351.3502	-1.6
7	1	7	6	1	6	8642.0823	-0.6
7	1	7	6	0	6	8662.2205	2.1
7	2	5	6	2	4	9907.8985	1.3
7	2	6	6	2	5	9186.3882	0.2
8	0	8	7	0	7	9841.507	1.3
8	0	8	7	1	7	9833.2238	-0.9
8	1	7	7	1	6	10513.3137	-1.6
8	1	8	7	1	7	9836.5146	0.2
8	1	8	7	0	7	9844.7947	-0.8
8	2	6	7	2	5	11207.0374	2.0
8	2	7	7	2	6	10414.2347	-1.3

Table S19. Measured transition lines for 1,7DSU···$(H_2O)_2$: Residual between observed frequency and that calculated (SPFIT) from the spectroscopic parameters (MHz), with the experimental accuracy of 0.005 MHz for all lines.

J'	Ka′	Kc′	J''	Ka′′	Kc′′	ν_{obs}/MHz	$\Delta\nu_{obs-calc}$/kHz
5	4	1	4	3	2	8185.2031	0.6
5	4	2	4	3	1	8164.5692	-1.3
5	4	2	4	3	2	8182.7697	-2.6
5	5	0	4	4	0	9000.4212	-1.1
5	5	1	4	4	1	9000.6685	-2.5
6	3	3	5	2	3	8228.2771	-4.5
6	3	4	5	2	4	8607.8315	1.0
6	4	2	5	3	2	9196.5059	-0.1
6	4	3	5	3	3	9254.1551	-1.6
6	5	1	5	4	1	10057.2296	1.1
6	5	2	5	4	1	10056.9534	2.3
6	5	2	5	4	2	10059.383	1.7
6	6	0	5	5	1	10881.7118	2.9
6	6	0	5	5	0	10881.6782	-5.2
6	6	1	5	5	0	10881.6782	-2.9
6	6	1	5	5	1	10881.7118	5.1
7	2	5	6	1	5	9044.3329	1.6
7	3	4	6	2	4	9254.0354	0.3
7	3	5	6	2	5	9809.7649	-1.6
7	4	3	6	3	4	10383.6995	-0.3
7	4	4	6	3	4	10342.2184	-0.3
7	5	2	6	4	3	11119.7031	3.9
7	5	2	6	4	2	11107.8754	3.3
7	5	3	6	4	2	11106.245	4.5
7	5	3	6	4	3	11118.0707	3.1
7	6	1	6	5	1	11940.0726	7.6
7	6	2	6	5	2	11940.3185	4.8
7	7	0	6	6	0	12761.9168	-9.6
7	7	1	6	6	1	12761.9168	-11.7
8	0	8	7	0	7	7765.3253	2.2
8	1	7	7	1	6	8275.3741	-0.7
8	1	8	7	1	7	7759.2958	1.3
8	2	6	7	2	5	8745.5747	-1.6
8	2	6	7	1	6	10439.7231	2.0
8	2	7	7	2	6	8176.2848	0.0
8	2	7	7	1	6	8393.1868	-2.9
8	2	7	7	1	7	11035.149	-2.4
8	3	5	7	3	4	8804.2484	1.8
8	3	5	7	2	5	10354.5067	-3.5
8	3	6	7	3	5	8450.624	-0.1
8	3	6	7	2	6	11057.7286	-5.5

8	4	4	7	4	3	8605.2868	1.5
8	4	4	7	3	4	11152.5544	-0.8
8	4	5	7	4	4	8530.7865	1.3
8	4	5	7	3	5	11456.9656	-1.8
8	5	3	7	5	2	8520.6826	4.9
9	0	9	8	0	8	8704.9788	1.8
9	0	9	8	1	8	8700.393	0.5
9	1	8	8	1	7	9195.9386	-1.0
9	1	9	8	1	8	8702.3237	0.9
9	1	9	8	0	8	8706.9068	-0.5
9	2	7	8	2	6	9737.2338	-1.2
9	2	8	8	2	7	9137.8113	0.9
9	3	6	8	3	5	9941.8367	2.4
9	3	6	8	2	6	11550.7669	-1.3
9	3	7	8	3	6	9467.5681	-0.3
9	4	5	8	4	4	9756.3412	0.6
9	4	6	8	4	5	9601.4785	-1.7
9	5	4	8	5	3	9614.9691	1.9
9	5	5	8	5	4	9598.8219	-1.3
10	0	10	9	0	9	9645.6009	0.4
10	0	10	9	1	9	9643.6686	-1.6
10	1	9	9	1	8	10121.5921	-1.2
10	1	9	9	2	8	10061.9112	3.6
10	1	10	9	1	9	9644.4662	-1.0
10	1	10	9	0	9	9646.398	0.5
10	2	8	9	2	7	10682.0149	-1.8
10	2	9	9	2	8	10090.6484	-0.4
10	3	7	9	3	6	11040.07	2.1
10	3	8	9	3	7	10466.105	-0.7
10	4	6	9	4	5	10932.1986	-0.5
10	4	7	9	4	6	10661.3115	-2.8
10	5	5	9	5	4	10726.6439	-7.0
10	5	6	9	5	5	10684.7759	-0.3
11	0	11	10	0	10	10586.6518	-0.7
11	1	10	10	1	9	11053.3342	-0.8
11	1	11	10	1	10	10586.1805	0.9
11	2	9	10	2	8	11597.9861	-0.9
11	2	9	10	3	8	11248.6542	7.5
11	2	10	10	2	9	11037.9232	-1.5
11	3	9	10	3	8	11447.4683	-1.1
12	0	12	11	0	11	11527.8609	-3.0
12	1	11	11	1	10	11989.3055	2.5
12	1	12	11	1	11	11527.6681	-1.9
12	2	10	11	2	9	12507.374	0.1

12	2	11	11	2	10	11981.9809	0.4
13	0	13	12	0	12	12469.105	-1.3
13	1	12	12	1	11	12927.6834	-0.1
13	1	13	12	1	12	12469.0308	2.9
13	2	12	12	2	11	12924.3239	1.4