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

Internal Dynamics of Cyclohexanol and the Cyclohexanol-Water Adduct

Electronic Supporting Information

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parameter describing the internal rotation of the OH group. τ = 0 corresponds to the B_2 barrier between the two gauche forms.

Table S15. B3LYP-GD3/6-311++G(d,p) and MP2/6-311++G(d,p) predictions for the dimer cyclohexanol ⋯ H_2O.

Table S16. Results of the effective structure determination for E_g-cyclohexanol⋯H_2O. The fitted parameters (r_0) are compared with the theoretical predictions (theory, B3LYP-D3/6-311++G(d,p)). The differences with the experimental rotational constants for the fitted structure are shown below.

Table S17. Substitution coordinates for the oxygen atom of E_g-cyclohexanol ⋯ H_2O using the Kraitchman equations (unsigned), and comparison with the DFT prediction (B3LYP-D3/6-311++G(d,p)).

Table S1: Experimental transition frequencies (ν, MHz) and observed-calculated values ($\Delta\nu$, kHz) for E_g-cyclohexanol.

	*E*g			
$J'_{Ka',Kc'}\leftarrow J''_{Ka'',Kc''}$	v=0←0		v=1←1	
	ν/MHz	$\Delta\nu$/kHz	ν/MHz	$\Delta\nu$/kHz
	μ_a-transitions			
1(0,1)-0(0,0)	3843.9155	-0.3		
2(1,2)-1(1,1)	7068.7561	-1.2	7069.2209	-0.9
2(0,2)-1(0,1)	7568.2542	-1.4	7568.7149	-1.3
2(1,1)-1(1,0)	8306.8594	1.0	8307.8554	-2.1
3(0,3)-2(0,2)	11080.2528	-0.7	11080.5176	-1.1
3(1,3)-2(1,2)	10534.4232	-1.5	10535.0049	0.0
3(1,2)-2(1,1)	12376.8066	0.9	12378.1345	-2.0
3(2,2)-2(2,1)	11531.6086	1.2	11532.9187	-0.7
3(2,1)-2(2,0)	11983.0899	0.3	11985.1662	0.4
4(0,4)-3(0,3)	14378.3233	-0.7	14378.3233	-3.5
4(1,4)-3(1,3)	13936.2153	0.1	13936.8462	1.9
4(1,3)-3(1,2)	16326.0807	-2.1	16327.4970	-3.6
4(2,3)-3(2,2)	15281.5953	-0.6	15283.1885	3.6
4(2,2)-3(2,1)	16277.3984	-1.3	16280.358	5.6
4(3,2)-3(3,1)	15576.5174	-0.2	15579.0876	-3.8
4(3,1)-3(3,0)	15662.8294	-0.1	15665.6800	1.8
5(0,5)-4(0,4)	17561.1911	-0.2	17561.1911	4.4
5(1,5)-4(1,4)	17277.518	-0.4	17278.1899	-2.9
	μ_c-transitions			
4(2,3)-4(1,3)	4303.2148	7.4		
3(2,2)-3(1,2)	5347.6953	1.0		
2(2,1)-2(1,1)	6192.8952	2.7		
1(1,0)-0(0,0)	6527.2717	2.8	6525.1762	1.2
1(1,1)-1(0,1)	2064.2962	-4.9		
2(1,1)-1(0,1)	10990.2147	3.2	10988.7729	-0.8
2(2,0)-1(1,0)	14619.326	2.1	14612.4376	2.2
2(2,1)-1(1,1)	15118.8033	0.4	15111.9518	-4.6
3(1,2)-2(0,2)	15798.7639	2.4	15798.1933	-0.7
3(2,1)-2(1,1)	18295.5563	1.2	18289.7472	3.5
3(3,0)-3(2,2)	11952.5875	-7.6		
5(2,4)-5(1,4)	3170.3234	-3.2		

Table S2. Experimental transition frequencies (ν, MHz) and observed-calculated values ($\Delta\nu$, kHz) for E_t-cyclohexanol.

E_t		
$J'_{Ka',Kc'} \leftarrow J''_{Ka'',Kc''}$	ν/MHz	$\Delta\nu$/kHz
μ_a-transitions		
2(1,2)-1(1,1)	7043.4031	-2.1
2(0,2)-1(0,1)	7535.1499	0.3
2(1,1)-1(1,0)	8256.3504	-2.4
3(0,3)-2(0,2)	11040.6686	0.1
3(1,3)-2(1,2)	10499.0808	0.4
3(1,2)-2(1,1)	12304.6340	-1.8
3(2,2)-2(2,1)	11474.8066	-0.6
3(2,1)-2(2,0)	11908.9463	-2.2
4(0,4)-3(0,3)	14336.9825	2.6
4(1,4)-3(1,3)	13893.0165	-0.53
4(1,3)-3(1,2)	16237.7715	-2.4
4(2,3)-3(2,2)	15209.7034	-0.5
4(2,2)-3(2,1)	16171.0686	-0.5
4(3,2)-3(3,1)	15493.4958	2.8
4(3,1)-3(3,0)	15574.6180	3.0
5(0,5)-4(0,4)	17516.9424	-1.1
5(1,5)-4(1,4)	17228.0282	-0.5
μ_c-transitions		
1(1,0)-0(0,0)	6503.8956	-0.1
2(1,1)-1(0,1)	10935.3066	-0.3
2(2,0)-1(1,0)	14588.5200	1.7
2(2,1)-1(1,1)	15080.2652	2.0
3(1,2)-2(0,2)	15704.7892	-4.0
3(2,1)-2(1,1)	18241.1196	5.5
2(2,0)-2(1,2)	8151.5951	7.2
3(3,1)-3(2,1)	11395.7131	-4.5
3(3,0)-3(2,2)	11958.4480	-1.5
4(3,1)-4(2,3)	12323.3581	-2.6

Table S3. Rotational parameters of the ^{13}C and ^{18}O monosubstituted species for E_g-cyclohexanol.

	E_g				
	^{18}O	$^{13}C(1)$	$^{13}C(2)$	$^{13}C(3)$	$^{13}C(4)$
A / MHz[a]	4295.2590(99)[c]	4292.1256(48)	4238.3882(23)	4237.9889(53)	4293.154(26)
B / MHz	2129.8380(76)	2221.0786(36)	2230.4242(17)	2217.0575(40)	2195.761(16)
C / MHz	1558.7562(41)	1607.5840(28)	1604.0619(14)	1597.2030(31)	1594.220(13)
D_J / kHz	[0.90][d]	[0.90]	[0.90]	[0.90]	[0.90]
D_{JK} / kHz	[5.16]	[5.16]	[5.16]	[5.16]	[5.16]
D_K / kHz	[0.36]	[0.36]	[0.36]	[0.36]	[0.36]
d_1 / kHz	[0.121]	[0.121]	[0.121]	[0.121]	[0.121]
d_2 / kHz	[0.00]	[0.00]	[0.00]	[0.00]	[0.00]
N[b]	4	6	6	6	5
σ / kHz	3.1	6.9	3.4	7.7	27.2

[a]Rotational constants (A, B, C), Watson's S-reduction centrifugal distortion constants (D_J, D_{JK}, D_K, d_1, d_2). [b]Number of transitions (N) and rms deviation (σ) of the fit. [c]Standard errors in parentheses in units of the last digit. [d]Values in square brackets were kept fixed in the fit.

Table S4. Measured rotational transitions of the ^{18}O isotopologue of E_g-cyclohexanol, residuals according to fit of Table S3 and assumed experimental uncertainties (all values in MHz).

J'	K_{-1}'	K_{+1}'	J''	K_{-1}''	K_{+1}''	Frequency	Residuals	Uncertainty
1	0	1	0	0	0	3688.5858	-0.0048	0.020
1	1	0	0	0	0	6425.0827	-0.0001	0.020
2	1	2	1	1	1	6806.0517	-0.0014	0.020
2	0	2	1	0	1	7278.3589	0.0038	0.020

Table S5. Measured rotational transitions of the $^{13}C(1)$ isotopologue of E_g-cyclohexanol, residuals according to fit of Table S3 and assumed experimental uncertainties (all values in MHz).

J'	K_{-1}'	K_{+1}'	J''	K_{-1}''	K_{+1}''	Frequency	Residuals	Uncertainty
1	0	1	0	0	0	3828.6567	-0.0023	0.020
3	2	2	3	1	2	5374.4555	0.0049	0.020
2	2	1	2	1	1	6213.0332	-0.0050	0.020
1	1	0	0	0	0	6513.1903	0.0000	0.020
2	1	2	1	1	1	7043.7670	-0.0102	0.020
2	0	2	1	0	1	7540.0352	0.0114	0.020

Table S6. Measured rotational transitions of the ^{13}C(2) isotopologue of E_g-cyclohexanol, residuals according to fit of Table S3 and assumed experimental uncertainties (all values in MHz).

J'	K_{-1}'	K_{+1}'	J''	K_{-1}''	K_{+1}''	Frequency	Residuals	Uncertainty
1	0	1	0	0	0	3834.4860	0.0035	0.020
3	2	2	3	1	2	5171.8354	0.0014	0.020
2	2	1	2	1	1	6023.7885	-0.0008	0.020
1	1	0	0	0	0	6468.7967	-0.0019	0.020
2	1	2	1	1	1	7042.5510	-0.0054	0.020
2	0	2	1	0	1	7543.8620	0.0046	0.020

Table S7. Measured rotational transitions of the $^{13}C(3)$ isotopologue of E_g-cyclohexanol, residuals according to fit of Table S3 and assumed experimental uncertainties (all values in MHz).

J'	K_{-1}'	K_{+1}'	J''	K_{-1}''	K_{+1}''	Frequency	Residuals	Uncertainty
1	0	1	0	0	0	3814.2443	-0.0126	0.020
3	2	2	3	1	2	5218.1959	-0.0057	0.020
2	2	1	2	1	1	6062.6984	0.0070	0.020
1	1	0	0	0	0	6455.0281	-0.0045	0.020
2	1	2	1	1	1	7008.6122	-0.0009	0.020
2	0	2	1	0	1	7506.4659	0.0095	0.020

Table S8. Measured rotational transitions of the ^{13}C(4) isotopologue of E_g-cyclohexanol, residuals according to fit of Table S3 and assumed experimental uncertainties (all values in MHz).

J'	K_{-1}'	K_{+1}'	J''	K_{-1}''	K_{+1}''	Frequency	Residuals	Uncertainty
1	0	1	0	0	0	3790.0090	0.0300	0.020
3	2	2	3	1	2	5467.3910	0.0059	0.020
1	1	0	0	0	0	6488.8835	-0.0189	0.020
2	1	2	1	1	1	6978.3330	-0.0373	0.020
2	0	2	1	0	1	7468.1044	0.0317	0.020

Table S9. Rotational parameters of the E_g-cyclohexanol ⋯ $H_2{}^{16}O$ and E_g-cyclohexanol ⋯ $H_2{}^{18}O$.

	E_g-Cyclohexanol ⋯ H_2O			
	Cyclohexanol ⋯ $H_2{}^{16}O$		Cyclohexanol ⋯ $H_2{}^{18}O$	
	0^+ state	0^- state	0^+ state	0^- state
A / MHz[a]	2555.2943(21)[d]	2556.2312(50)	2512.5849(25)	2510.8384(48)
B / MHz	1130.35883(48)	1129.94502(59)	1081.8941(10)	1081.4645(14)
C / MHz	1113.24155(43)	1112.60936(75)	1073.8764(10)	1073.2330(17)
D_J / kHz	-1.3293(57)		[-0.0013293][e]	
D_{JK} / kHz	2.75(13)		[0.00275]	
D_K / kHz	-6.87(24)		[-0.00687]	
d_1 / Hz	0.1375(26)		[0.1375]	
d_2 / Hz	0.0449(42)		[0.0449]	
ΔE / MHz[b]	32672(354)		[32672]	
F_{ab} / MHz	15.63(14)		[15.63]	
F_{bc} / MHz	5.850(50)		[5.850]	
N[b]	74		20	
σ / kHz	7.2		8.7	

[a]Rotational constants (A, B, C) and Watson's S-reduction centrifugal distortion constants (D_J, D_{JK}, D_K, d_1, d_2). [b]Torsional energy difference (ΔE) and coupling terms (F_{ab} and F_{bc}). [b]Number of transitions (N) and rms deviation (σ) of the fit. [d]Standard errors in parentheses in units of the last digit. [e]Values in square brackets were kept fixed in the fit.

Table S10. Measured rotational transitions of E_g-Cyclohexanol ⋯ H_2O, residuals according to fit of Table S9 and assumed experimental uncertainties (all values in MHz).

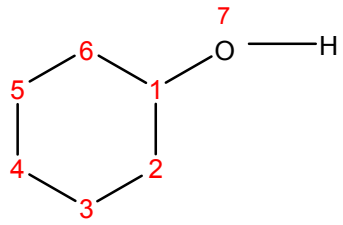
J'	K_{-1}'	K_{+1}'	v'	J''	K_{-1}''	K_{+1}''	v''	Frequency	Residuals	Uncertainty
1	0	1	0	0	0	0	0	2243.5840	-0.0039	0.023
2	0	2	0	1	1	0	0	3044.9317	0.0095	0.023
1	1	0	0	0	0	0	0	3685.6331	-0.0128	0.023
1	1	0	1	0	0	0	1	3686.1784	0.0072	0.023
6	2	5	0	6	1	5	0	4119.8403	0.0098	0.023
5	2	4	0	5	1	4	0	4171.4411	0.0033	0.023
4	2	3	0	4	1	3	0	4214.4688	0.0041	0.023
4	2	3	1	4	1	3	1	4219.2543	0.0074	0.023
3	2	2	0	3	1	2	0	4248.8903	-0.0055	0.023
2	2	1	0	2	1	1	0	4274.7161	-0.0071	0.023
2	2	0	0	2	1	2	0	4326.2586	-0.0198	0.023
3	2	1	0	3	1	3	0	4352.5295	-0.0054	0.023
4	2	2	0	4	1	4	0	4388.3663	-0.0016	0.023
5	2	3	0	5	1	5	0	4434.4892	0.0087	0.023
2	1	2	1	1	1	1	1	4467.8208	-0.0168	0.023
2	1	2	0	1	1	1	0	4469.9651	0.0009	0.023
2	0	2	1	1	0	1	1	4484.9498	0.0102	0.023
2	0	2	0	1	0	1	0	4486.9766	-0.0035	0.023
6	2	4	0	6	1	6	0	4491.7548	0.0099	0.023
2	1	1	1	1	1	0	1	4502.5080	0.0048	0.023
2	1	1	0	1	1	0	0	4504.2214	-0.0015	0.023
4	1	4	0	3	2	2	0	4587.5887	0.0123	0.023
4	1	3	0	3	2	1	0	4758.0727	-0.0023	0.023
3	0	3	1	2	1	1	1	5265.8028	0.0070	0.023
3	0	3	0	2	1	1	0	5270.6845	0.0042	0.023
2	1	1	1	1	0	1	1	5946.1118	-0.0056	0.023
2	1	1	0	1	0	1	0	5946.2689	-0.0121	0.023
3	1	3	1	2	1	2	1	6701.6137	0.0042	0.023
3	1	3	0	2	1	2	0	6704.7361	-0.0008	0.023
3	0	3	1	2	0	2	1	6726.9782	0.0046	0.023
3	0	3	0	2	0	2	0	6729.9762	-0.0049	0.023
3	2	2	0	2	2	1	0	6730.3119	-0.0009	0.023
3	2	1	0	2	2	0	0	6731.0006	0.0070	0.023
3	1	2	1	2	1	1	1	6753.6268	0.0039	0.023
3	1	2	0	2	1	1	0	6756.1369	-0.0031	0.023
5	1	5	0	4	2	3	0	6787.6446	0.0056	0.023
5	1	4	0	4	2	2	0	7042.1584	-0.0101	0.023

7	3	5	0	7	2	5	0	7149.5533	-0.0001	0.023
6	3	4	0	6	2	4	0	7157.0516	-0.0134	0.023
5	3	3	0	5	2	3	0	7161.9519	0.0113	0.023
5	3	2	0	5	2	4	0	7167.9447	0.0106	0.023
6	3	3	0	6	2	5	0	7169.0965	0.0112	0.023
7	3	4	0	7	2	6	0	7171.2355	-0.0165	0.023
7	3	4	0	7	2	6	0	7171.2494	-0.0026	0.023
4	0	4	1	3	1	2	1	7480.6628	0.0052	0.023
4	0	4	0	3	1	2	0	7486.9375	0.0026	0.023
4	1	4	0	3	1	3	0	8939.2609	0.0005	0.010
4	0	4	1	3	0	3	1	8968.4800	-0.0047	0.010
4	0	4	0	3	0	3	0	8972.3899	-0.0047	0.010
4	1	3	0	3	1	2	0	9007.8191	-0.0028	0.010
5	0	5	0	4	1	3	0	9693.1250	-0.0128	0.010
4	1	3	1	3	0	3	1	10492.4100	-0.0003	0.005
5	1	5	1	4	1	4	1	11168.5704	0.0008	0.005
5	1	5	0	4	1	4	0	11173.4544	0.0011	0.005
5	0	5	1	4	0	4	1	11209.2994	0.0002	0.005
5	0	5	0	4	0	4	0	11214.0217	-0.0033	0.005
5	2	4	0	4	2	3	0	11216.1638	0.0039	0.005
5	3	3	0	4	3	2	0	11216.5900	-0.0137	0.010
5	3	2	0	4	3	2	0	11216.6459	0.0082	0.005
5	2	3	0	4	2	2	0	11219.5719	0.0061	0.005
5	1	4	1	4	1	3	1	11255.3304	0.0013	0.005
5	1	4	0	4	1	3	0	11259.1855	-0.0012	0.005
5	1	4	1	4	0	4	1	12779.2545	-0.0001	0.005
6	1	6	1	5	1	5	1	13401.6436	-0.0013	0.005
6	1	6	0	5	1	5	0	13407.2386	0.0014	0.005
6	0	6	0	5	0	5	0	13454.6771	-0.0013	0.005
6	4	2	0	5	4	1	0	13458.2200	0.0036	0.005
6	4	3	0	5	4	2	0	13458.2200	0.0040	0.005
6	2	5	0	5	2	4	0	13458.5437	0.0009	0.005
6	3	4	0	5	3	3	0	13459.6169	-0.0091	0.005
6	3	3	0	5	3	2	0	13459.6865	-0.0074	0.005
6	1	5	0	5	1	4	0	13510.1510	0.0009	0.005
7	1	7	0	6	1	6	0	15640.5380	0.0021	0.005
7	0	7	0	6	0	6	0	15694.1652	0.0000	0.005
7	1	6	0	6	1	5	0	15760.6254	0.0021	0.005

Table S11. Measured rotational transitions of E_g-Cyclohexanol ⋯ $H_2{}^{18}O$, residuals according to fit of Table S9 and assumed experimental uncertainties (all values in MHz).

J'	K_{-1}'	K_{+1}'	v'	J''	K_{-1}''	K_{+1}''	v''	Frequency [1]	Residuals	Uncertainty
2	2	1	0	2	1	1	0	4291.9993	0.0102	0.023
2	1	2	0	1	1	1	0	4303.3998	-0.0043	0.023
2	0	2	0	1	0	1	0	4311.4384	-0.0017	0.023
2	1	1	0	1	1	0	0	4319.4692	0.0054	0.023
3	2	1	0	3	1	3	0	4328.1674	-0.0140	0.023
4	2	2	0	4	1	4	0	4344.4752	-0.0018	0.023
5	2	3	0	5	1	5	0	4365.2177	0.0148	0.023
3	0	3	0	2	1	1	0	5020.2370	0.0044	0.023
2	1	1	0	1	0	1	0	5758.1544	-0.0230	0.023
3	1	3	0	2	1	2	0	6454.9804	0.0098	0.023
3	0	3	0	2	0	2	0	6466.9728	0.0029	0.023
3	1	2	0	2	1	1	0	6479.0746	-0.0014	0.023
4	2	3	1	4	1	3	1	4260.1466	0.0020	0.023
2	1	2	1	1	1	1	1	4301.2261	-0.0018	0.023
2	0	2	1	1	0	1	1	4309.3562	0.0084	0.023
2	1	1	1	1	1	0	1	4317.6889	0.0035	0.023
2	1	1	1	1	0	1	1	5755.2769	-0.0062	0.023
3	1	3	1	2	1	2	1	6451.7617	-0.0094	0.023
3	0	3	1	2	0	2	1	6463.8972	0.0066	0.023
3	1	2	1	2	1	1	1	6476.4738	0.0002	0.023

Table S12. Substitution coordinates for the oxygen and carbon atoms of E_g cyclohexanol using Kraitchman equations (unsigned), and comparison with the ab initio prediction (MP2/6-311++G(d,p)).



E_g Cyclohexanol			
	a / Å[a]	***b*** / Å	***c*** / Å
O(7)	2.34368(64)[b]	[0.][c]	0.0894(169)
C(1)	0.97929 (154)	[0.]	0.3304 (46)
C(2)	0.2730(55)	1.25365(120)	0.1825(82)
C(3)	1.19064(127)	1.26095(120)	0.2147(71)
C(4)	1.90247(80)	[0.]	0.3002(50)
C(5)	1.19064(127)	1.26095(120)	0.2147(71)
C(6)	0.2730(55)	1.25365(120)	0.1825(82)
		MP2/ 6-311++G(d,p)	
O(7)	-2.343	0.051	-0.106
C(1)	-0.984	-0.008	0.330
C(2)	-0.297	1.250	-0.177
C(3)	1.184	1.263	0.219
C(4)	1.900	0.009	-0.290
C(5)	1.203	-1.259	0.214
C(6)	-0.277	-1.258	-0.185

[a]Principal inertial axes denoted *a*, *b*, *c*. [b]Uncertainties according to Costain's estimation: $\delta z = 0.0015/z$. [c]Imaginary value, fixed to zero.

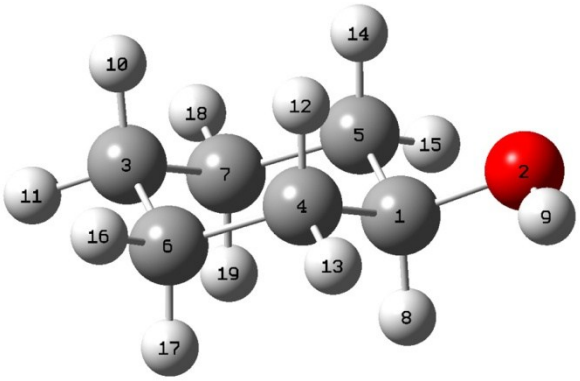
Table S13. Effective structure determination for E_g cyclohexanol and theoretical predictions (B3LYP-D3/6-311++G(d,p)). The differences with the experimental rotational constants are shown below.

Fitted Parameters[a]	r_0	theory
α(C2-C1-O7) / deg	106.57(1.05)	107.11
α(C3-C2-C1) / deg	111.41(39)	110.92
α(C4-C3-C2) / deg	111.08(45)	111.04
α(C5-C4-C3) / deg	109.03(79)	110.83
α(C6-C5-C5) / deg	111.156(37)	110.72
τ(C3-C2-C1-O7) / deg	-178.33(1.30)	-178.81
τ(C4-C3-C2-C1) / deg	55.57(37)	56.30
τ(C5-C4-C3-C2) / deg	-56.84(61)	-55.87
r (C1-O7) / Å	1.429(5)	1.430
r (C2-C1) / Å	1.529(17)	1.521
r (C3-C2) / Å	1.532(6)	1.532
r (C4-C3) / Å	1.550(6)	1.532

Isotopic species	Axis	Experiment / MHz	Exp.-Calc. / MHz
Parent	*A*	4295.78841	0.01
	B	2231.48431	0.00
	C	1612.43425	0.01
^{18}O(7)	*A*	4295.2590	-0.75
	B	2129.8380	-0.00
	C	1558.7562	0.03
^{13}C(1)	*A*	4292.1256	-0.01
	B	2221.0786	-0.04
	C	1607.5840	-0.09
^{13}C(2)	*A*	4238.3882	0.01
	B	2230.4242	-0.00
	C	1604.0619	-0.09
^{13}C(3)	*A*	4237.9889	-0.22
	B	2217.0575	-0.11
	C	1597.2030	-0.02
^{13}C(4)	*A*	4293.1540	-0.98
	B	2195.7610	-0.45
	C	1594.2206	-0.25
^{13}C(5)	*A*	4237.9889	-0.15
	B	2217.0575	-0.07
	C	1597.2030	-0.04
^{13}C(6)	*A*	4238.3882	-0.03
	B	2230.4242	-0.04

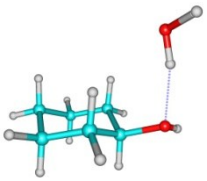
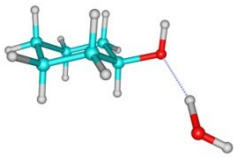
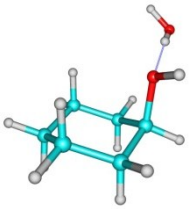
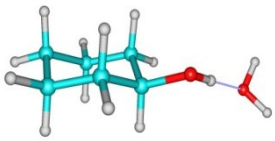
	C	1604.0619	-0.09
RMS residuals			0.27

Table S14. Schematic description of the structural relaxations taken into account in the flexible model calculations for the conformers pair E_g/E_t of the monomer of cyclohexanol, and structural relaxations of the other parameters upon internal rotation of the hydroxyl group. τ (H9O2-C1H8) is the parameter describing the internal rotation of the OH group. τ = 0 corresponds to the B_2 barrier between the two gauche forms.



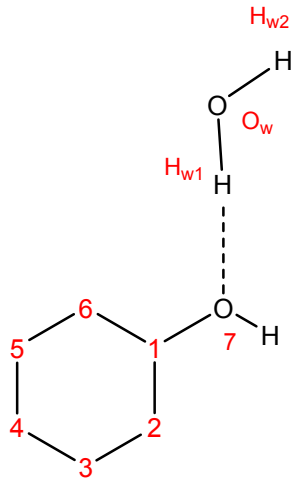
C3C1-O2H9=180-τ
C4C1-C3O2=74.7+4.7·sin τ
C5C1-C3O2=-74.7+4.7·sin τ
C3C1O2=148.9+2.8·(1-cos τ)
C6C4C1O2=-183.8+2.6·(1+cos τ)
C7C5C1O2=183.8-2.6·(1+cos τ)

Table S15. B3LYP-GD3/6-311++G(d,p) and MP2/6-311++G(d,p) predictions for the dimer cyclohexanol ⋯ H_2O.

	E_g (acceptor)	*E_t (acceptor)*	*A_g (acceptor)*	*E_g (donor)*
				
A / MHz[a]	2532.23/2553.7	3235.79/3183.0	2916.02/2958.39	3428.92/3432.36
B / MHz	1172.05/1166.6	1067.67/1071.1	1194.59/1187.90	979.13/982.71
C / MHz	1153.51/1139.8	868.76/889.1	1012.27/1010.99	808.64/812.83
D_J / kHz	0.9967/1.2539	0.5502/1.0563	1.2023/0.7632	0.6871/0.4806
D_{JK} / kHz	-1.5513/-2.5120	-2.6793/-5.4214	-2.8631/-0.4905	-3.0256/-1.6166
D_K / kHz	2.7740/4.4893	7.8137/14.2428	15.3843/7.9900	10.1654/7.5455
d_1 / kHz	0.0974/0.1451	-0.0947/-0.1390	-0.2172/-0.1431	-0.1878/-0.1174
d_2 / kHz	0.0385/0.0123	-0.0111/0.0182	-0.0138/-0.0111	-0.0169/-0.0133
$\lvert\mu_a\rvert$ / D	0.92/1.80	2.06/1.40	2.88/1.38	2.57/1.15
$\lvert\mu_b\rvert$ / D	0.03/0.64	1.39/0.86	1.05/2.69	1.72/1.52
$\lvert\mu_c\rvert$ / D	1.86/0.89	0.39/1.94	0.67/0.30	0.42/2.47
ΔE / kJ mol^{-1} [b]	0.00/0.00	0.95/1.11	3.20/2.98	6.12/3.72
ΔG / kJ mol^{-1}	0.00/0.13	0.03/0.00	1.30/2.52	1.75/0.44

[a]Rotational constants (*A*, *B*, *C*), Watson's S-reduction centrifugal distortion constants (D_J, D_{JK}, D_K, d_1, d_2) and electric dipole moments (μ_α, α = a, b, c). [b]Relative energies corrected with the zero-point energy (ZPE), Gibbs energy (ΔG, 298K, 1 atm) and complexation energy (including BSSE corrections). [c]B3LYP-GD3 / MP2 values, respectively (basis set 6-311++G(d,p)).

Table S16. Results of the effective structure determination for E_g cyclohexanol···H_2O. The fitted parameters (r_0) are compared with the theoretical predictions (theory, B3LYP-D3/6-311++G(d,p)). The differences with the experimental rotational constants for the fitted structure are shown below.



Fitted Parameters[a]	r_0	theory
α(H_{w1}-O7-C1) / deg	110.645(80)	107.618
r (O7-H_{w1}) / Å	1.928(5)	1.881

Isotopic species	Axis	Experiment / MHz	Exp.-Calc. / MHz
Parent	*A*	2555.29430	5.65
	B	1130.35883	1.13
	C	1113.24155	1.12
^{18}O(7)	*A*	2512.58490	7.09
	B	1081.89410	2.99
	C	1073.87640	3.05
RMS residuals			3.95

Table S17. Substitution coordinates for the oxygen atom in E_g cyclohexanol ⋯ H_2O using the Kraitchman equations (unsigned), and comparison with the DFT prediction (B3LYP-D3/6-311++G(d,p)).

	E_g Cyclohexanol – water		
	a / Å[a]	***b*** / Å	***c*** / Å
O_w	2.88780(52)[b]	[0.0][c]	134714(111)
	B3LYL-GD3/ 6-311++G(d,p)		
O_w	-2.741579	0.191460	1.385945

[a]Principal inertial axes denoted *a*, *b*, *c*. [a]Uncertainties according to Costain's estimation: δz=0.0015/z. [c]Imaginary value, fixed to zero.