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

Supporting Information for :

Microhydration of verbenone : how the chain of water molecules adapts its structure to the host molecule

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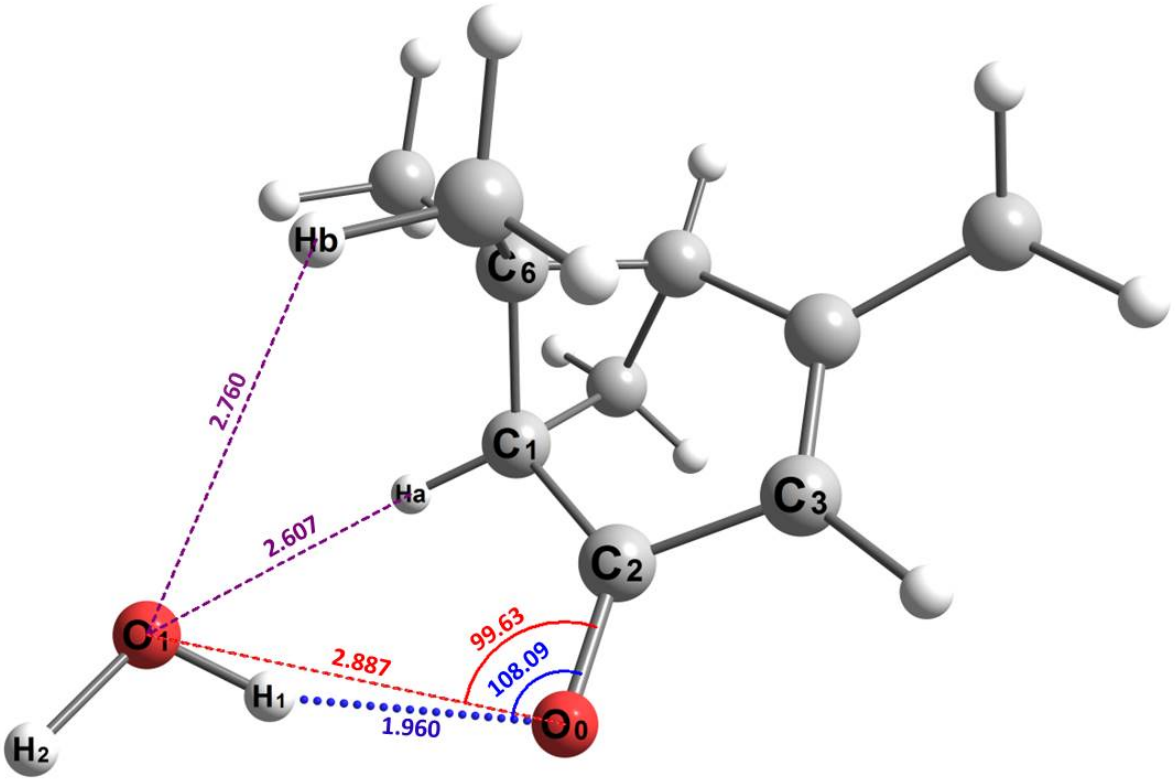


Figure S1: Optimized structure (MP2/6-311++G(d,p)) of the 1w-I complex of verbenone with one water molecule. Distances in Å, angles in °. The purple dashed lines indicate the shortest distances between the water oxygen atom and some hydrogen atoms of verbenone.

Table S1: Experimental rotational and quartic centrifugal distortion constants of the normal and of the $H_2^{18}O$ substituted species of the 1w-I hydrate of verbenone.

	Normal	$^{18}O_1$
A/MHz	1219.960 64(36)	1219.124 44(20)
B/MHz	763.384 24(10)	734.209 684(43)
C/MHz	608.198 816(63)	589.681 732(39)
Δ_J/kHz	0.262 09(55)	0.265 62(25)
Δ_{JK}/kHz	0.0286(26)	0.0145(31)
Δ_K/kHz	−0.1345(48)	[b]
δ_J/kHz	0.024 54(20)	[b]
δ_K/kHz	0.1004(29)	[b]
N_{lines} [a]	67	49
σ_{fit} (kHz)	1.39	0.83
$P_a(u.\text{Å}^2)$	539.355 00(6)	565.412 464(7)
$P_b(u.\text{Å}^2)$	291.588 72(6)	291.624 438(7)
$P_c(u.\text{Å}^2)$	122.669 48(6)	122.918 153(7)

[a] The number of fitted lines ; [b] Fixed at the value of the normal species.

Table S2: Experimental coordinates (in Å, in the principal axes systems) of the water oxygen atom O_1 in the 1w-I hydrate of verbenone, along with those obtained by *ab initio* and DFT calculations.

	a	*b*	*c*
r_s/ Å	−3.6258(1)	−0.1413(18)	0.3652(7)
r_0/ Å	−3.6249(11)	−0.1846(8)	0.3622(4)
MP2 [a]/ Å	−3.492	−0.214	0.411
DFT [b]/ Å	−3.556	−0.211	0.341

[a] MP2 / 6-311++G(d,p) ; [b] B3LYP-D3BJ / def2-TZVP.

Table S3: Effective and quantum chemistry parameters of the verbenone monohydrate 1w-I.

Parameters [a]	r_0 [b]	r_0 [c]	B3LYP [d]	MP2 [e]
$r(O_0O_1)$/ Å	3.0148(10)	3.0126(12)	2.833	2.887
$\angle(H_1O_1O_0)$/ °	29.5(12)	34.0(14)	11.4	13.8
$\angle(O_1O_0C_2)$/ °	98.963(22)	98.988(21)	102.5	99.6
$\tau(O_1O_0C_2C_1)$/ °	145.834(18)	145.790(16)	145.0	141.6
σ_{fit}/uÅ^2	0.015	0.015	-	-

[a] The numbering scheme is shown Fig. S1 ; additional parameters involving the H atoms taken from the : [b] MP2/6-311++G(d,p) [c] B3LYP-D3BJ/def2-TZVP geometries ; [d] B3LYP-D3BJ / def2-TZVP ; [e] 6-311++G(d,p).

Table S4: Measured frequencies ($\nu_{\text{obs.}}$) and residuals ($\nu_{\text{obs.}} - \nu_{\text{calc.}}$) in MHz of the monohydrate of verbenone 1w-I.

J'	K'_a	K'_c	$\leftarrow$	J''	K''_a	K''_c	$\nu_{\text{obs.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	exp. error
							$^aR_{0,1}$ transitions		
3	0	3	$\leftarrow$	2	0	2	3990.5570	−0.0004	0.001
3	1	3	$\leftarrow$	2	1	2	3862.9660	0.0000	0.001
3	1	2	$\leftarrow$	2	1	1	4323.9257	0.0002	0.001
4	0	4	$\leftarrow$	3	0	3	5217.7312	0.0000	0.001
4	1	4	$\leftarrow$	3	1	3	5120.8510	−0.0008	0.001
4	1	3	$\leftarrow$	3	1	2	5714.9227	−0.0002	0.001
4	2	3	$\leftarrow$	3	2	2	5460.0764	0.0014	0.001
4	2	2	$\leftarrow$	3	2	1	5728.0881	0.0012	0.001
5	0	5	$\leftarrow$	4	0	4	6420.9223	−0.0004	0.001
5	1	5	$\leftarrow$	4	1	4	6363.2179	0.0000	0.001
5	1	4	$\leftarrow$	4	1	3	7052.2727	0.0000	0.001
5	2	4	$\leftarrow$	4	2	3	6784.1007	0.0000	0.001
5	2	3	$\leftarrow$	4	2	2	7216.8687	0.0003	0.001
5	3	3	$\leftarrow$	4	3	2	6932.5543	−0.0004	0.001
5	3	2	$\leftarrow$	4	3	1	7019.3449	−0.0010	0.001
6	0	6	$\leftarrow$	5	0	5	7623.3072	−0.0002	0.001
6	1	6	$\leftarrow$	5	1	5	7594.0392	0.0000	0.001
6	1	5	$\leftarrow$	5	1	4	8322.7758	0.0006	0.001
6	2	5	$\leftarrow$	5	2	4	8084.0698	−0.0001	0.001
6	2	4	$\leftarrow$	5	2	3	8672.2974	0.0002	0.001
6	3	4	$\leftarrow$	5	3	3	8314.1635	−0.0008	0.001
6	3	3	$\leftarrow$	5	3	2	8515.9670	0.0004	0.001
6	4	3	$\leftarrow$	5	4	2	8337.0848	0.0005	0.004
6	4	2	$\leftarrow$	5	4	1	8354.8165	−0.0017	0.002
7	0	7	$\leftarrow$	6	0	6	8831.0439	−0.0006	0.001
7	1	7	$\leftarrow$	6	1	6	8817.5947	0.0004	0.001
7	1	6	$\leftarrow$	6	1	5	9536.3199	0.0008	0.001
7	2	6	$\leftarrow$	6	2	5	9360.0192	−0.0001	0.001
7	2	5	$\leftarrow$	6	2	4	10 074.3617	0.0008	0.001

J'	K'_a	K'_c	←	J''	K''_a	K''_c	$\nu_{\text{obs.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	exp. error
7	3	5	←	6	3	4	9678.0555	0.0003	0.001
7	4	4	←	6	4	3	9746.2294	−0.0009	0.001
7	4	3	←	6	4	2	9801.5056	−0.0022	0.001
8	0	8	←	7	0	7	10 042.9643	−0.0008	0.001
8	1	8	←	7	1	7	10 037.1573	0.0003	0.001
8	1	7	←	7	1	6	10 724.3391	0.0004	0.001
8	2	7	←	7	2	6	10 614.9242	0.0001	0.001
8	3	6	←	7	3	5	11 018.0338	−0.0001	0.001
8	4	5	←	7	4	4	11 152.4909	−0.0008	0.001
8	5	4	←	7	5	3	11 134.7410	0.0030	0.001
9	0	9	←	8	0	8	11 257.1473	−0.0002	0.001
9	1	9	←	8	1	8	11 254.7437	0.0009	0.001
9	2	7	←	8	2	6	12 666.0703	0.0005	0.001
10	0	10	←	9	0	9	12 472.3775	−0.0053	0.001
10	1	10	←	9	1	9	12 471.4211	0.0040	0.001
10	1	9	←	9	1	8	13 111.2113	−0.0002	0.001
10	2	9	←	9	2	8	13 081.7838	0.0003	0.001
10	2	8	←	9	2	7	13 864.0008	−0.0008	0.001
10	3	8	←	9	3	7	13 616.6035	0.0000	0.001
10	4	7	←	9	4	6	13 923.2730	−0.0003	0.001
							$^{b}R_{-1,1}$ transitions		
6	0	6	←	5	1	5	7570.7957	−0.0006	0.001
6	1	5	←	5	2	4	7685.2656	−0.0003	0.002
8	0	8	←	7	1	7	10 033.1718	−0.0007	0.001
8	1	7	←	7	2	6	10 501.8347	0.0003	0.001
9	0	9	←	8	1	8	11 253.1606	−0.0025	0.004
9	1	8	←	8	2	7	11 800.0594	0.0000	0.002
10	0	10	←	9	1	9	12 470.8025	−0.0007	0.002

J'	K'_a	K'_c	$\leftarrow$	J''	K''_a	K''_c	$\nu_{\text{obs.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	exp. error
							$^bR_{1,-1}$ transitions		
5	3	2	$\leftarrow$	4	2	3	9821.6659	−0.0004	0.001
5	5	0	$\leftarrow$	4	4	1	11 671.0628	0.0022	0.002
6	5	1	$\leftarrow$	5	4	2	13 054.1982	−0.0011	0.002
							$^bR_{1,1}$ transitions		
5	5	1	$\leftarrow$	4	4	0	11 670.4846	0.0001	0.002
6	1	6	$\leftarrow$	5	0	5	7646.5502	−0.0001	0.001
6	5	2	$\leftarrow$	5	4	1	13 048.9990	−0.0009	0.002
8	1	8	$\leftarrow$	7	0	7	10 046.9509	0.0013	0.001
8	2	7	$\leftarrow$	7	1	6	10 837.4285	0.0000	0.001
9	1	9	$\leftarrow$	8	0	8	11 258.7310	0.0037	0.002
9	2	8	$\leftarrow$	8	1	7	11 966.8270	−0.0003	0.001
10	1	10	$\leftarrow$	9	0	9	12 472.9994	0.0027	0.002

Table S5: Measured frequencies ($\nu_{\text{obs.}}$) and residuals ($\nu_{\text{obs.}} - \nu_{\text{calc.}}$) in MHz of the monohydrate of verbenone 1w-I labeled with ^{18}O.

J'	K'_a	K'_c	←	J''	K''_a	K''_c	$\nu_{\text{obs.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	exp. error
							$^{a}R_{0,1}$ transitions		
4	0	4	←	3	0	3	5063.5258	0.0001	0.001
4	1	4	←	3	1	3	4959.6635	−0.0002	0.001
4	1	3	←	3	1	2	5517.8208	0.0001	0.001
5	0	5	←	4	0	4	6233.1934	−0.0003	0.001
5	1	5	←	4	1	4	6166.3118	−0.0007	0.001
5	1	4	←	4	1	3	6822.9498	0.0008	0.001
5	2	4	←	4	2	3	6557.8153	0.0007	0.001
5	2	3	←	4	2	2	6941.2226	0.0011	0.001
6	0	6	←	5	0	5	7398.4478	−0.0009	0.001
6	1	6	←	5	1	5	7361.8125	−0.0005	0.001
6	1	5	←	5	1	4	8070.8351	0.0028	0.002
6	2	5	←	5	2	4	7821.2776	0.0001	0.002
7	0	7	←	6	0	6	8567.8955	−0.0004	0.002
7	1	7	←	6	1	6	8549.7863	0.0000	0.002
8	0	8	←	7	0	7	9741.6818	−0.0008	0.001
8	1	8	←	7	1	7	9733.2962	0.0000	0.001
8	1	7	←	7	1	6	10 421.1854	−0.0004	0.001
8	2	7	←	7	2	6	10 285.8151	−0.0005	0.001
8	2	6	←	7	2	5	11 039.5925	−0.0002	0.001
8	3	6	←	7	3	5	10 645.9884	0.0004	0.001
8	3	5	←	7	3	4	11 107.6798	−0.0002	0.001
8	4	5	←	7	4	4	10 748.4610	0.0004	0.001
8	4	4	←	7	4	3	10 843.3815	0.0002	0.001
9	0	9	←	8	0	8	10 918.1329	−0.0010	0.001
9	1	9	←	8	1	8	10 914.4182	0.0013	0.001
9	1	8	←	8	1	7	11 572.3379	−0.0003	0.001
9	2	8	←	8	2	7	11 492.1428	−0.0003	0.001
9	2	7	←	8	2	6	12 288.8698	−0.0006	0.001
9	3	7	←	8	3	6	11 926.2501	0.0000	0.001
9	3	6	←	8	3	5	12 548.6817	−0.0004	0.001

J'	K'_a	K'_c	$\leftarrow$	J''	K''_a	K''_c	$\nu_{\text{obs.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	exp. error
9	4	6	$\leftarrow$	8	4	5	12 099.0097	0.0005	0.001
9	4	5	$\leftarrow$	8	4	4	12 297.4518	−0.0004	0.001
10	0	10	$\leftarrow$	9	0	9	12 095.9450	−0.0014	0.001
10	1	10	$\leftarrow$	9	1	9	12 094.3524	0.0024	0.001
10	1	9	$\leftarrow$	9	1	8	12 729.8642	0.0000	0.002
10	2	9	$\leftarrow$	9	2	8	12 686.8105	0.0000	0.001
10	3	8	$\leftarrow$	9	3	7	13 182.3770	−0.0007	0.001
11	0	11	$\leftarrow$	10	0	10	13 274.3797	−0.0059	0.005
11	1	11	$\leftarrow$	10	1	10	13 273.7233	0.0073	0.005
							$^bR_{-1,1}$ transitions		
9	0	9	$\leftarrow$	8	1	8	10 911.6882	−0.0009	0.002
10	0	10	$\leftarrow$	9	1	9	12 093.2145	−0.0041	0.005
10	1	9	$\leftarrow$	9	2	8	12 646.3649	−0.0011	0.002
							$^bR_{1,-1}$ transitions		
5	5	0	$\leftarrow$	4	4	1	11 638.6703	0.0018	0.002
							$^bR_{1,1}$ transitions		
5	5	1	$\leftarrow$	4	4	0	11 638.2892	−0.0015	0.002
8	3	6	$\leftarrow$	7	2	5	12 179.8675	0.0002	0.002
9	1	9	$\leftarrow$	8	0	8	10 920.8635	0.0018	0.001
9	2	8	$\leftarrow$	8	1	7	11 655.8373	0.0008	0.002
10	1	10	$\leftarrow$	9	0	9	12 097.0813	0.0036	0.005
10	2	9	$\leftarrow$	9	1	8	12 770.3098	0.0010	0.002

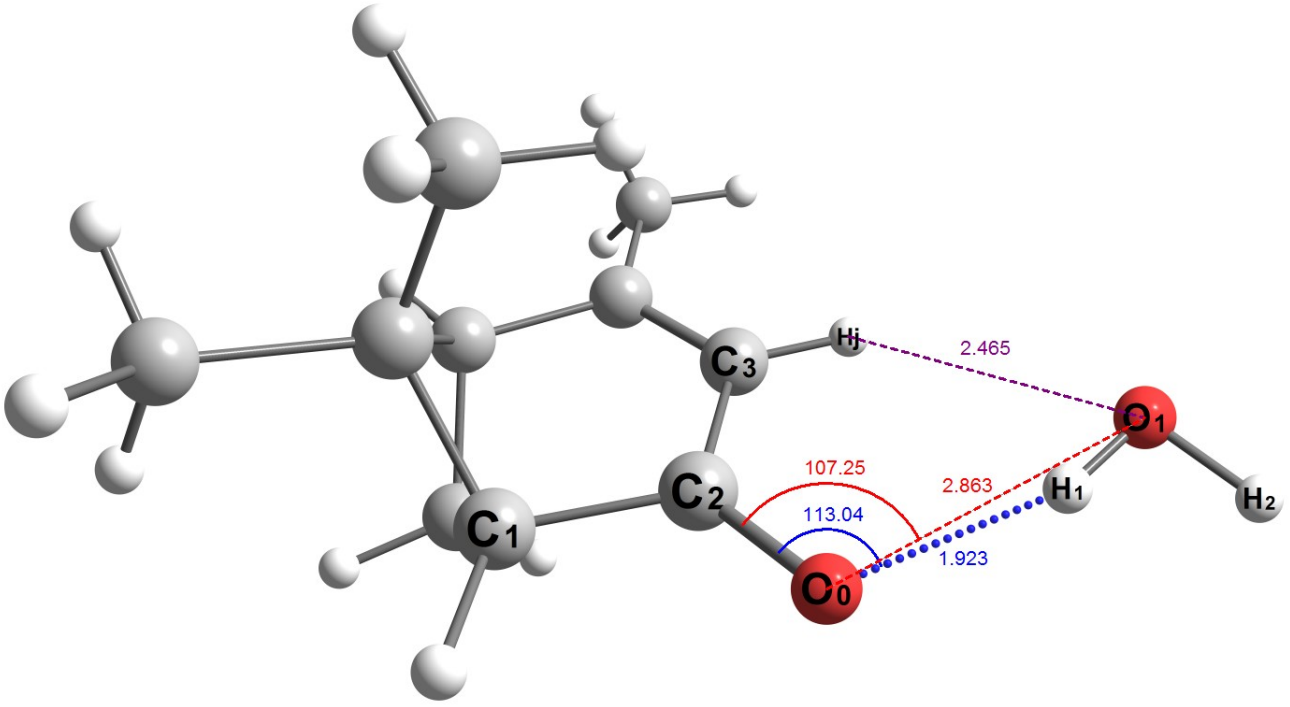


Figure S2: Optimized structure (MP2/6-311++G(d,p)) of the 1w-II complex of verbenone with one water molecule. Distances in Å, angles in °. The purple dashed lines indicate the shortest distances between the water oxygen atom and some hydrogen atoms of verbenone.

Table S6: Experimental rotational and quartic centrifugal distortion constants of the normal and of $H_2^{18}O$ substituted species of the 1w-II hydrate of verbenone.

	Normal	$^{18}O_1$
A/MHz	1253.750 46(10)	1252.784 91(24)
B/MHz	666.514 908(72)	637.345 110(14)
C/MHz	554.132 012(38)	533.944 104 2(80)
Δ_J/kHz	0.091 94(40)	[b]
Δ_{JK}/kHz	0.0880(26)	[b]
Δ_K/kHz	-	-
δ_J/kHz	0.007 50(21)	[b]
δ_K/kHz	−0.0693(48)	[b]
N_{lines}[a]	68	50
σ_{fit} (kHz)	0.82	0.40
$P_a(u.\text{Å}^2)$	633.583 242(7)	668.020 647(6)
$P_b(u.\text{Å}^2)$	278.435 905(7)	278.481 058(6)
$P_c(u.\text{Å}^2)$	124.657 870(7)	124.923 390(6)

[a] The number of fitted lines ; [b] Fixed at the value of the normal species.

Table S7: Experimental coordinates (in Å, in the principal axes systems) of the water oxygen atom O_1 in the 1w-II complex of verbenone, along with those obtained by *ab initio* and DFT calculations.

	a	*b*	*c*
r_s/ Å	4.1684(4)	0.1580(95)	−0.3784(40)
r_0/ Å	4.1662(21)	0.1719(5)	−0.4154(6)
MP2 [a]/ Å	4.111	0.171	−0.436
DFT [b]/ Å	4.111	0.186	−0.419

[a] MP2 / 6-311++G(d,p) ; [b] B3LYP-D3BJ / def2-TZVP.

Table S8: Effective and quantum chemistry parameters of verbenone monohydrate 1w-II.

Parameters [a]	r_0 [b]	B3LYP [c]	MP2 [d]
$r(O_0O_1)$/ Å	2.8646(18)	2.827	2.863
$\angle(O_1O_0C_2)$/ °	109.736(67)	108.1	107.2
$\angle(H_1O_1O_0)$/ °	19.9(21)	9.2	11.6
$\tau(O_1O_0C_2C_1)$/ °	2.578(31)	1.95	3.52
σ_{fit}/uÅ^2	0.036	-	-

[a] the numbering scheme is shown Fig. S2. [b] additional parameters involving the H atoms taken from the MP2/6-311++G(d,p) optimized geometry; [c] B3LYP-D3BJ / def2-TZVP; [d] 6-311++G(d,p).

Table S9: Measured frequencies ($\nu_{\text{obs.}}$) and residuals ($\nu_{\text{obs.}} - \nu_{\text{calc.}}$) in MHz of the monohydrate of verbenone 1w-II.

J'	K'_a	K'_c	$\leftarrow$	J''	K''_a	K''_c	$\nu_{\text{obs.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	exp. error
					$^aR_{0,1}$ transitions				
3	0	3	$\leftarrow$	2	0	2	3604.9514	−0.0013	0.001
3	1	3	$\leftarrow$	2	1	2	3484.7342	0.0000	0.001
3	1	2	$\leftarrow$	2	1	1	3820.6778	−0.0002	0.001
4	0	4	$\leftarrow$	3	0	3	4749.0332	−0.0004	0.001
4	1	3	$\leftarrow$	3	1	2	5074.1769	0.0012	0.001
4	2	2	$\leftarrow$	3	2	1	5004.5763	0.0003	0.002
5	0	5	$\leftarrow$	4	0	4	5864.2267	0.0000	0.001
5	1	5	$\leftarrow$	4	1	4	5769.4600	−0.0003	0.001
5	1	4	$\leftarrow$	4	1	3	6306.9710	−0.0002	0.001
5	2	4	$\leftarrow$	4	2	3	6070.7020	0.0004	0.001
5	2	3	$\leftarrow$	4	2	2	6309.0124	0.0001	0.001
6	0	6	$\leftarrow$	5	0	5	6964.3032	0.0002	0.001
6	1	6	$\leftarrow$	5	1	5	6898.4305	−0.0002	0.001
6	1	5	$\leftarrow$	5	1	4	7510.5829	0.0002	0.001
6	2	5	$\leftarrow$	5	2	4	7258.6946	−0.0003	0.001
6	2	4	$\leftarrow$	5	2	3	7615.3011	−0.0004	0.001
6	3	4	$\leftarrow$	5	3	3	7375.1529	0.0010	0.001
6	3	3	$\leftarrow$	5	3	2	7437.2357	−0.0001	0.001
7	0	7	$\leftarrow$	6	0	6	8061.2516	0.0001	0.001
7	1	7	$\leftarrow$	6	1	6	8020.2600	−0.0002	0.001
7	1	6	$\leftarrow$	6	1	5	8677.7577	0.0000	0.001
7	2	6	$\leftarrow$	6	2	5	8433.7348	0.0001	0.001
7	2	5	$\leftarrow$	6	2	4	8907.4529	−0.0002	0.001
7	3	5	$\leftarrow$	6	3	4	8604.2684	−0.0001	0.001
7	3	4	$\leftarrow$	6	3	3	8733.1592	0.0000	0.001
7	4	4	$\leftarrow$	6	4	3	8613.7370	0.0042	0.004
8	0	8	$\leftarrow$	7	0	7	9160.4613	−0.0002	0.001
8	1	8	$\leftarrow$	7	1	7	9136.8215	−0.0002	0.001

J'	K'_a	K'_c	$\leftarrow$	J''	K''_a	K''_c	$\nu_{\text{obs.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	exp. error
						[a] $R_{0,1}$ transitions			
8	1	7	$\leftarrow$	7	1	6	9807.5060	0.0002	0.001
8	2	7	$\leftarrow$	7	2	6	9595.2950	0.0004	0.001
8	2	6	$\leftarrow$	7	2	5	10 174.7709	0.0004	0.001
8	3	6	$\leftarrow$	7	3	5	9825.8690	−0.0001	0.001
8	3	5	$\leftarrow$	7	3	4	10 053.1402	−0.0006	0.001
8	4	5	$\leftarrow$	7	4	4	9857.9085	0.0014	0.001
8	4	4	$\leftarrow$	7	4	3	9882.9346	0.0003	0.001
9	0	9	$\leftarrow$	8	0	8	10 262.7824	−0.0001	0.001
9	1	9	$\leftarrow$	8	1	8	10 249.8385	0.0002	0.001
9	1	8	$\leftarrow$	8	1	7	10 908.6953	0.0007	0.001
9	2	8	$\leftarrow$	8	2	7	10 743.8528	−0.0003	0.001
9	2	7	$\leftarrow$	8	2	6	11 409.6440	0.0008	0.002
9	3	7	$\leftarrow$	8	3	6	11 036.6881	−0.0004	0.001
9	3	6	$\leftarrow$	8	3	5	11 385.8028	0.0006	0.002
9	4	6	$\leftarrow$	8	4	5	11 103.2043	0.0000	0.001
9	4	5	$\leftarrow$	8	4	4	11 160.0821	0.0000	0.001
9	5	4	$\leftarrow$	8	5	3	11 084.7974	−0.0011	0.001
10	0	10	$\leftarrow$	9	0	9	11 367.4795	−0.0006	0.001
10	1	10	$\leftarrow$	9	1	9	11 360.6467	0.0004	0.001
10	1	9	$\leftarrow$	9	1	8	11 996.2316	0.0000	0.001
10	2	9	$\leftarrow$	9	2	8	11 880.8367	0.0000	0.001
11	0	11	$\leftarrow$	10	0	10	12 473.6717	−0.0020	0.001
11	1	11	$\leftarrow$	10	1	10	12 470.1623	0.0009	0.001
12	1	12	$\leftarrow$	11	1	11	13 578.9564	0.0009	0.001
						[b] $R_{-1,1}$ transitions			
6	0	6	$\leftarrow$	5	1	5	6807.0410	−0.0005	0.001
7	0	7	$\leftarrow$	6	1	6	7969.8617	−0.0005	0.001
8	0	8	$\leftarrow$	7	1	7	9110.0627	−0.0008	0.001
8	1	7	$\leftarrow$	7	2	6	9139.7781	−0.0008	0.004
9	0	9	$\leftarrow$	8	1	8	10 236.0233	−0.0010	0.001
9	1	8	$\leftarrow$	8	2	7	10 453.1775	−0.0014	0.002

J'	K'_a	K'_c	$\leftarrow$	J''	K''_a	K''_c	$\nu_{\text{obs.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	exp. error
10	0	10	$\leftarrow$	9	1	9	11 353.6650	−0.0012	0.002
							$^bR_{1,1}$ transitions		
3	3	1	$\leftarrow$	2	2	0	6873.0410	−0.0009	0.001
4	4	1	$\leftarrow$	3	3	0	9388.1430	0.0008	0.002
6	1	6	$\leftarrow$	5	0	5	7055.6928	0.0006	0.001
7	1	7	$\leftarrow$	6	0	6	8111.6505	0.0010	0.001
9	1	9	$\leftarrow$	8	0	8	10 276.5975	0.0010	0.001
10	1	10	$\leftarrow$	9	0	9	11 374.4618	0.0017	0.002
							$^bR_{1,-1}$ transitions		
3	3	0	$\leftarrow$	2	2	1	6888.8871	0.0024	0.001
4	4	0	$\leftarrow$	3	3	1	9389.4211	−0.0071	0.002
5	3	2	$\leftarrow$	4	2	3	9438.0574	0.0004	0.002

Table S10: Measured frequencies ($\nu_{\text{obs.}}$) and residuals ($\nu_{\text{obs.}} - \nu_{\text{calc.}}$) in MHz of the monohydrate of verbenone 1w-II labeled with ^{18}O.

J'	K'_a	K'_c	$\leftarrow$	J''	K''_a	K''_c	$\nu_{\text{obs.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	exp. error
					$^aR_{0,1}$ transitions				
3	0	3	$\leftarrow$	2	0	2	3467.0216	0.0008	0.002
3	1	2	$\leftarrow$	2	1	1	3660.9949	0.0000	0.001
4	0	4	$\leftarrow$	3	0	3	4574.0206	0.0003	0.002
4	1	4	$\leftarrow$	3	1	3	4456.7972	0.0000	0.001
4	1	3	$\leftarrow$	3	1	2	4865.2090	−0.0007	0.001
5	0	5	$\leftarrow$	4	0	4	5653.9429	0.0001	0.001
5	1	5	$\leftarrow$	4	1	4	5553.8408	0.0001	0.001
5	1	4	$\leftarrow$	4	1	3	6053.0198	−0.0007	0.001
5	2	4	$\leftarrow$	4	2	3	5829.8365	0.0013	0.002
5	2	3	$\leftarrow$	4	2	2	6031.8732	−0.0001	0.001
6	0	6	$\leftarrow$	5	0	5	6717.1390	0.0000	0.001
6	1	6	$\leftarrow$	5	1	5	6643.1031	0.0000	0.001
6	1	5	$\leftarrow$	5	1	4	7217.6447	0.0000	0.001
6	2	5	$\leftarrow$	5	2	4	6974.3027	−0.0008	0.002
6	2	4	$\leftarrow$	5	2	3	7282.9528	−0.0003	0.002
6	3	4	$\leftarrow$	5	3	3	7071.9088	0.0005	0.002
6	3	3	$\leftarrow$	5	3	2	7117.7332	0.0003	0.002
7	0	7	$\leftarrow$	6	0	6	7774.7245	0.0004	0.001
7	1	7	$\leftarrow$	6	1	6	7725.6776	−0.0004	0.001
7	1	6	$\leftarrow$	6	1	5	8352.4358	0.0000	0.001
7	2	6	$\leftarrow$	6	2	5	8107.9063	0.0011	0.002
7	2	5	$\leftarrow$	6	2	4	8525.9609	−0.0003	0.001
7	3	4	$\leftarrow$	6	3	3	8349.1770	−0.0004	0.002
8	0	8	$\leftarrow$	7	0	7	8833.0850	0.0000	0.001
8	1	8	$\leftarrow$	7	1	7	8803.0471	−0.0002	0.001
8	1	7	$\leftarrow$	7	1	6	9454.1122	0.0000	0.001
8	2	7	$\leftarrow$	7	2	6	9229.9347	0.0000	0.001
8	2	6	$\leftarrow$	7	2	5	9750.5979	0.0006	0.001
8	3	5	$\leftarrow$	7	3	4	9602.9154	−0.0002	0.001

J'	K'_a	K'_c	$\leftarrow$	J''	K''_a	K''_c	$\nu_{\text{obs.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	exp. error
8	4	4	$\leftarrow$	7	4	3	9464.0256	−0.0006	0.002
9	0	9	$\leftarrow$	8	0	8	9894.1215	−0.0002	0.001
9	1	9	$\leftarrow$	8	1	8	9876.7017	0.0004	0.001
9	1	8	$\leftarrow$	8	1	7	10 526.4508	0.0008	0.001
9	2	8	$\leftarrow$	8	2	7	10 340.4266	0.0001	0.001
9	2	7	$\leftarrow$	8	2	6	10 949.9104	0.0005	0.001
10	0	10	$\leftarrow$	9	0	9	10 957.6143	−0.0004	0.001
10	1	10	$\leftarrow$	9	1	9	10 947.8935	0.0006	0.001
10	1	9	$\leftarrow$	9	1	8	11 580.1471	0.0002	0.001
10	2	9	$\leftarrow$	9	2	8	11 440.1870	−0.0007	0.001
10	3	8	$\leftarrow$	9	3	7	11 750.9510	0.0000	0.001
11	0	11	$\leftarrow$	10	0	10	12 022.8247	−0.0001	0.001
11	1	11	$\leftarrow$	10	1	10	12 017.5502	0.0003	0.001
12	1	12	$\leftarrow$	11	1	11	13 086.2962	0.0002	0.002
13	1	13	$\leftarrow$	12	1	12	14 154.5205	−0.0003	0.002
							$^bR_{1,1}$ transitions		
8	2	7	$\leftarrow$	7	1	6	10 028.6371	−0.0014	0.002
9	1	9	$\leftarrow$	8	0	8	9914.9056	0.0003	0.001
10	1	10	$\leftarrow$	9	0	9	10 968.6769	0.0004	0.002
							$^bR_{-1,1}$ transitions		
9	0	9	$\leftarrow$	8	1	8	9855.9176	−0.0001	0.002
10	0	10	$\leftarrow$	9	1	9	10 936.8301	−0.0011	0.001
10	1	9	$\leftarrow$	9	2	8	11 191.6442	0.0002	0.002

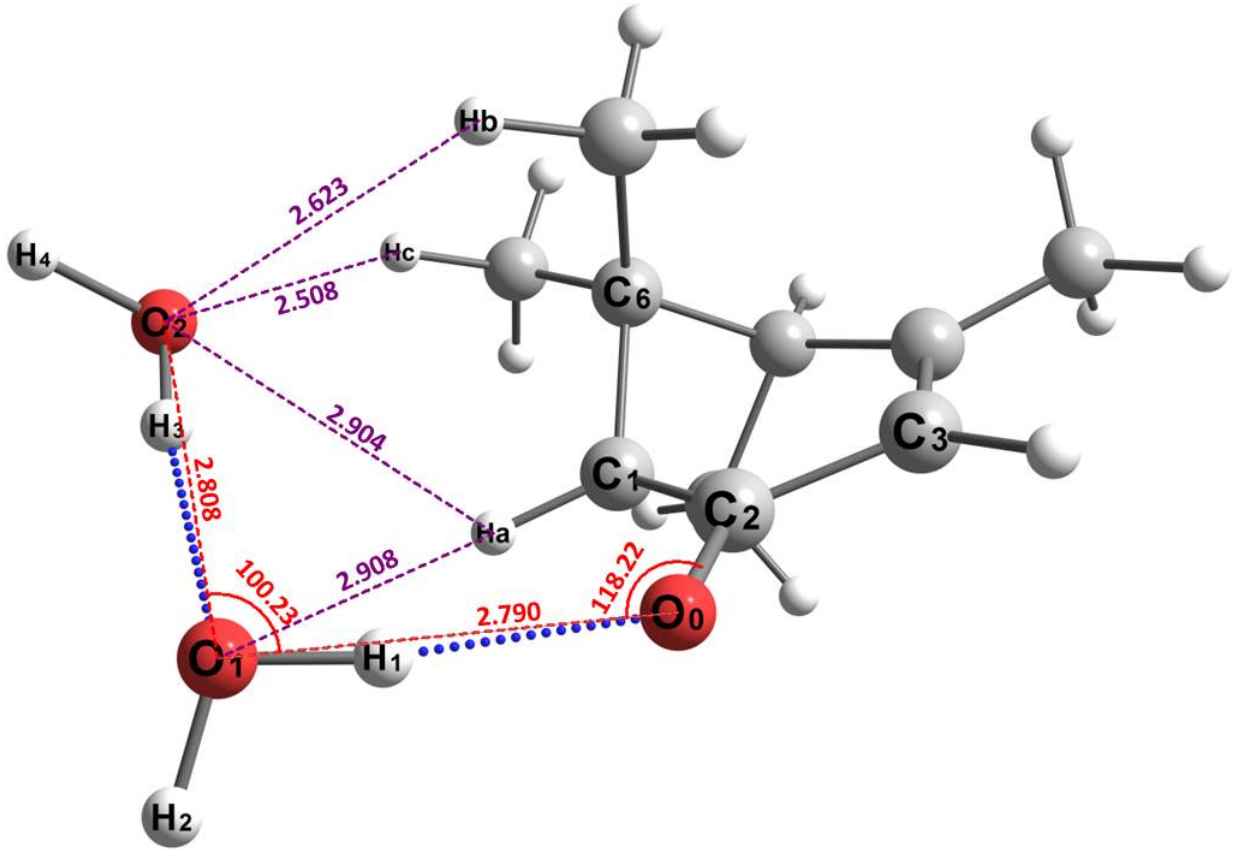


Figure S3: Optimized structure (MP2/6-311++G(d,p)) of the lowest energy conformer 2w-I of the dihydrates of verbenone. Distances in Å, angles in °. The purple dashed lines indicate the shortest distances between the water oxygen atom and some hydrogen atoms of verbenone.

Table S11: Experimental rotational and quartic centrifugal distortion constants of the normal and of the $H_2^{18}O$ substituted species of the dihydrate of verbenone 2w-I.

	Normal	$^{18}O_1$-$^{18}O_2$	$^{18}O_1$-$^{16}O_2$	$^{16}O_1$-$^{18}O_2$
A (MHz)	1043.330 07(54)	1026.164 71(20)	1035.063 66(67)	1035.282 18(52)
B (MHz)	546.942 431(65)	521.023 102(47)	532.890 852(28)	533.960 235(23)
C (MHz)	437.078 352(28)	417.925 917(48)	426.700 375(22)	427.726 445(19)
Δ_J (kHz)	0.040 43(33)	0.039 65(33)	[b]	[b]
Δ_{JK} (kHz)	0.2593(22)	0.2683(34)	[b]	[b]
Δ_K (kHz)	−0.202(22)	[b]	[b]	[b]
δ_J(kHz)	0.005 25(16)	[b]	[b]	[b]
δ_K(kHz)	0.1095(32)	[b]	[b]	[b]
N_{lines} [a]	74	50	30	25
σ_{fit} (kHz)	0.62	0.85	0.60	0.43
$P_a(u.\text{Å}^2)$	797.9419(2)	843.3681(1)	822.2510(2)	819.9323(2)
$P_b(u.\text{Å}^2)$	358.3245(2)	365.8869(1)	362.1374(2)	361.6150(2)
$P_c(u.\text{Å}^2)$	126.0658(2)	126.6062(1)	126.1214(2)	126.5408(2)

[a] The number of fitted lines ; [b] Fixed at the value of the normal species.

Table S12: Experimental coordinates (in Å, in the principal axes systems) of the water oxygen atoms O_1 and O_2 in the 2w-I complex of verbenone, along with those obtained by *ab initio* and DFT calculations.

	a	*b*	*c*
		O_1	
r_s/ Å	−3.4860(4)	−1.4243(11)	−0.1719(87)
r_0/ Å	−3.501(10)	−1.446(22)	−0.069(2)
MP2 [a]/ Å	−3.518	−1.405	−0.076
DFT [b]/ Å	−3.440	−1.421	−0.093
		O_2	
r_s/ Å	−3.3165(5)	1.3187(11)	0.501(3)
r_0/ Å	−3.332(10)	1.348(15)	0.456(3)
MP2[a]/ Å	−3.274	1.336	0.480
DFT[b]/ Å	−3.271	1.300	0.481

[a] MP2 / 6-311++G(d,p) ; [b] B3LYP-D3BJ / def2-TZVP ;

Table S13: The substitution and effective structural parameters of the verbenone dihydrate 2w-I compared with those optimized by quantum chemistry.

Parameters [a]	r_s	r_0 [b]	B3LYP [c]	MP2 [d]
$r(O_1O_0)$/ Å	-	2.79(13)	2.742	2.790
$r(O_2O_1)$/ Å	2.848(36)	2.842(28)	2.786	2.808
$\angle(O_1O_0C_2)$/ °	-	118.3(40)	117.4	118.2
$\angle(O_2O_1O_0)$/ °	-	101.38(68)	101.6	100.3
$\tau(O_2O_1O_0C_2)$/ °	-	−22.40(60)	−25.2	−23.2
σ_{fit}/u$Å^2$	-	0.199	-	-

[a] The numbering scheme is shown Fig. S3; [b] Parameters involving the H atoms taken from the MP2/6-311++G(d,p) optimized geometry ; [c] B3LYP-D3BJ / def2-TZVP ; [d] MP2/6-311++G(d,p).

Table S14: Measured frequencies ($\nu_{\text{obs.}}$) and residuals ($\nu_{\text{obs.}} - \nu_{\text{calc.}}$) in MHz of the dihydrate of verbenone 2w-I.

J'	K'_a	K'_c	$\leftarrow$	J''	K''_a	K''_c	$\nu_{\text{obs.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	exp. error
					$^aR_{0,1}$ transitions				
3	0	3	$\leftarrow$	2	0	2	2889.1083	0.0011	0.001
3	1	3	$\leftarrow$	2	1	2	2777.7332	0.0009	0.001
4	0	4	$\leftarrow$	3	0	3	3790.9144	0.0001	0.001
4	1	4	$\leftarrow$	3	1	3	3687.8382	−0.0006	0.001
4	1	3	$\leftarrow$	3	1	2	4118.2373	−0.0003	0.002
5	0	5	$\leftarrow$	4	0	4	4666.0191	0.0013	0.001
5	1	5	$\leftarrow$	4	1	4	4588.1778	0.0004	0.001
5	1	4	$\leftarrow$	4	1	3	5106.8041	−0.0009	0.001
5	2	4	$\leftarrow$	4	2	3	4883.9257	0.0010	0.001
5	2	3	$\leftarrow$	4	2	2	5137.0456	−0.0011	0.002
5	3	2	$\leftarrow$	4	3	1	4992.5562	−0.0009	0.001
6	0	6	$\leftarrow$	5	0	5	5530.1203	0.0004	0.001
6	1	6	$\leftarrow$	5	1	5	5479.8724	0.0001	0.001
6	1	5	$\leftarrow$	5	1	4	6062.0603	−0.0004	0.001
6	2	5	$\leftarrow$	5	2	4	5831.8456	0.0004	0.001
6	2	4	$\leftarrow$	5	2	3	6201.6407	0.0002	0.001
6	3	4	$\leftarrow$	5	3	3	5957.5633	0.0008	0.001
6	3	3	$\leftarrow$	5	3	2	6034.4639	0.0002	0.001
7	0	7	$\leftarrow$	6	0	6	6393.9444	0.0001	0.001
7	1	7	$\leftarrow$	6	1	6	6364.8726	0.0007	0.001
7	1	6	$\leftarrow$	6	1	5	6977.8440	0.0001	0.001
7	2	6	$\leftarrow$	6	2	5	6765.8623	0.0001	0.001
7	2	5	$\leftarrow$	6	2	4	7246.4904	0.0000	0.001
7	3	5	$\leftarrow$	6	3	4	6947.6578	0.0004	0.001
7	3	4	$\leftarrow$	6	3	3	7103.2635	−0.0014	0.001
8	0	8	$\leftarrow$	7	0	7	7260.8910	−0.0007	0.001
8	1	8	$\leftarrow$	7	1	7	7245.2500	−0.0004	0.001
8	1	7	$\leftarrow$	7	1	6	7857.7106	0.0005	0.001

J'	K'_a	K'_c	$\leftarrow$	J''	K''_a	K''_c	$\nu_{\text{obs.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	exp. error
8	2	7	$\leftarrow$	7	2	6	7685.8646	0.0000	0.001
8	2	6	$\leftarrow$	7	2	5	8261.5757	0.0001	0.001
8	3	6	$\leftarrow$	7	3	5	7928.2305	0.0001	0.001
8	3	5	$\leftarrow$	7	3	4	8192.8852	0.0000	0.001
8	4	5	$\leftarrow$	7	4	4	7972.5935	0.0009	0.001
8	4	4	$\leftarrow$	7	4	3	8008.0302	−0.0007	0.001
8	5	3	$\leftarrow$	7	5	2	7953.7472	−0.0005	0.002
9	0	9	$\leftarrow$	8	0	8	8130.7495	−0.0005	0.001
9	1	9	$\leftarrow$	8	1	8	8122.7370	0.0000	0.001
9	1	8	$\leftarrow$	8	1	7	8715.8410	−0.0002	0.001
9	2	8	$\leftarrow$	8	2	7	8592.9433	0.0002	0.001
9	2	7	$\leftarrow$	8	2	6	9239.0745	0.0003	0.002
9	3	7	$\leftarrow$	8	3	6	8896.0066	0.0002	0.002
9	3	6	$\leftarrow$	8	3	5	9286.0363	0.0000	0.002
9	4	6	$\leftarrow$	8	4	5	8980.7236	0.0001	0.002
9	4	5	$\leftarrow$	8	4	4	9059.7170	0.0006	0.002
10	0	10	$\leftarrow$	9	0	9	9002.5187	−0.0012	0.002
10	1	10	$\leftarrow$	9	1	9	8998.5541	−0.0002	0.002
10	1	9	$\leftarrow$	9	1	8	9568.1799	0.0000	0.002
10	2	9	$\leftarrow$	9	2	8	9489.1625	−0.0003	0.002
11	0	11	$\leftarrow$	10	0	10	9875.3803	−0.0018	0.002
11	1	11	$\leftarrow$	10	1	10	9873.4688	−0.0004	0.002
11	1	10	$\leftarrow$	10	1	9	10 423.9361	−0.0004	0.001
11	2	10	$\leftarrow$	10	2	9	10 377.0745	−0.0005	0.001
11	3	9	$\leftarrow$	10	3	8	10 785.6422	0.0003	0.001
12	0	12	$\leftarrow$	11	0	11	10 748.8235	−0.0026	0.002
12	1	12	$\leftarrow$	11	1	11	10 747.9223	0.0008	0.001
13	0	13	$\leftarrow$	12	0	12	11 622.5643	−0.0031	0.002
13	1	13	$\leftarrow$	12	1	12	11 622.1458	−0.0005	0.001

J'	K'_a	K'_c	$\leftarrow$	J''	K''_a	K''_c	$\nu_{\text{obs.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	exp. error
14	1	14	$\leftarrow$	13	1	13	12 496.2647	0.0018	0.001
							$^{b}R_{-1,1}$ transitions		
6	0	6	$\leftarrow$	5	1	5	5419.5887	0.0002	0.001
7	0	7	$\leftarrow$	6	1	6	6333.6604	0.0000	0.001
8	0	8	$\leftarrow$	7	1	7	7229.6800	−0.0003	0.001
8	1	7	$\leftarrow$	7	2	6	7382.2827	−0.0001	0.002
9	0	9	$\leftarrow$	8	1	8	8115.1793	−0.0005	0.002
9	1	8	$\leftarrow$	8	2	7	8412.2604	0.0008	0.002
11	0	11	$\leftarrow$	10	1	10	9871.7888	−0.0017	0.002
11	1	10	$\leftarrow$	10	2	9	10 322.2700	−0.0001	0.002
12	0	12	$\leftarrow$	11	1	11	10 747.1469	−0.0006	0.002
							$^{b}R_{1,1}$ transitions		
4	4	1	$\leftarrow$	3	3	0	7796.9756	0.0001	0.002
6	1	6	$\leftarrow$	5	0	5	5590.4036	0.0000	0.001
7	1	7	$\leftarrow$	6	0	6	6425.1555	−0.0001	0.001
8	1	8	$\leftarrow$	7	0	7	7276.4614	−0.0004	0.001
9	1	9	$\leftarrow$	8	0	8	8138.3079	0.0007	0.002
11	1	11	$\leftarrow$	10	0	10	9877.0627	0.0019	0.002
							$^{b}R_{1,-1}$ transitions		
4	4	0	$\leftarrow$	3	3	1	7798.6256	−0.0004	0.002

Table S15: Measured frequencies ($\nu_{\text{obs.}}$) and residuals ($\nu_{\text{obs.}} - \nu_{\text{calc.}}$) in MHz of the dihydrate of verbenone 2w-I with the $^{16}O_1$ atom substituted by a ^{18}O atom.

J'	K'_a	K'_c	←	J''	K''_a	K''_c	$\nu_{\text{obs.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	exp. error
					$^aR_{0,1}$ transitions				
4	0	4	←	3	0	3	3702.5449	−0.0009	0.001
4	1	4	←	3	1	3	3599.3804	−0.0003	0.002
4	1	3	←	3	1	2	4016.0675	−0.0009	0.001
5	0	5	←	4	0	4	4558.5207	−0.0010	0.002
5	1	5	←	4	1	4	4478.8764	−0.0005	0.001
5	1	4	←	4	1	3	4982.3962	−0.0002	0.001
5	2	4	←	4	2	3	4764.3693	−0.0005	0.002
5	2	3	←	4	2	2	5002.9758	−0.0013	0.001
6	0	6	←	5	0	5	5402.6921	−0.0005	0.001
6	1	6	←	5	1	5	5350.0467	−0.0005	0.001
6	1	5	←	5	1	4	5918.0182	0.0008	0.001
6	2	5	←	5	2	4	5690.3799	−0.0009	0.001
6	2	4	←	5	2	3	6041.6269	−0.0002	0.001
7	0	7	←	6	0	6	6245.8187	−0.0002	0.001
7	1	7	←	6	1	6	6214.6463	0.0001	0.001
7	1	6	←	6	1	5	6816.5596	−0.0002	0.001
7	2	6	←	6	2	5	6603.3282	−0.0002	0.001
7	2	5	←	6	2	4	7062.9937	0.0004	0.001
7	3	4	←	6	3	3	6915.4851	0.0001	0.001
8	0	8	←	7	0	7	7091.7565	0.0002	0.001
8	1	8	←	7	1	7	7074.6115	0.0001	0.001
8	1	7	←	7	1	6	7679.8995	0.0001	0.001
8	2	7	←	7	2	6	7502.9668	0.0003	0.001
8	2	6	←	7	2	5	8057.2882	0.0012	0.002
8	3	5	←	7	3	4	7974.9090	0.0024	0.002
9	0	9	←	8	0	8	7940.5801	0.0001	0.001
9	1	9	←	8	1	8	7931.6096	0.0007	0.001
9	1	8	←	8	1	7	8520.1210	0.0025	0.005
9	2	8	←	8	2	7	8390.1461	0.0010	0.002
9	3	7	←	8	3	6	8678.1816	0.0017	0.002

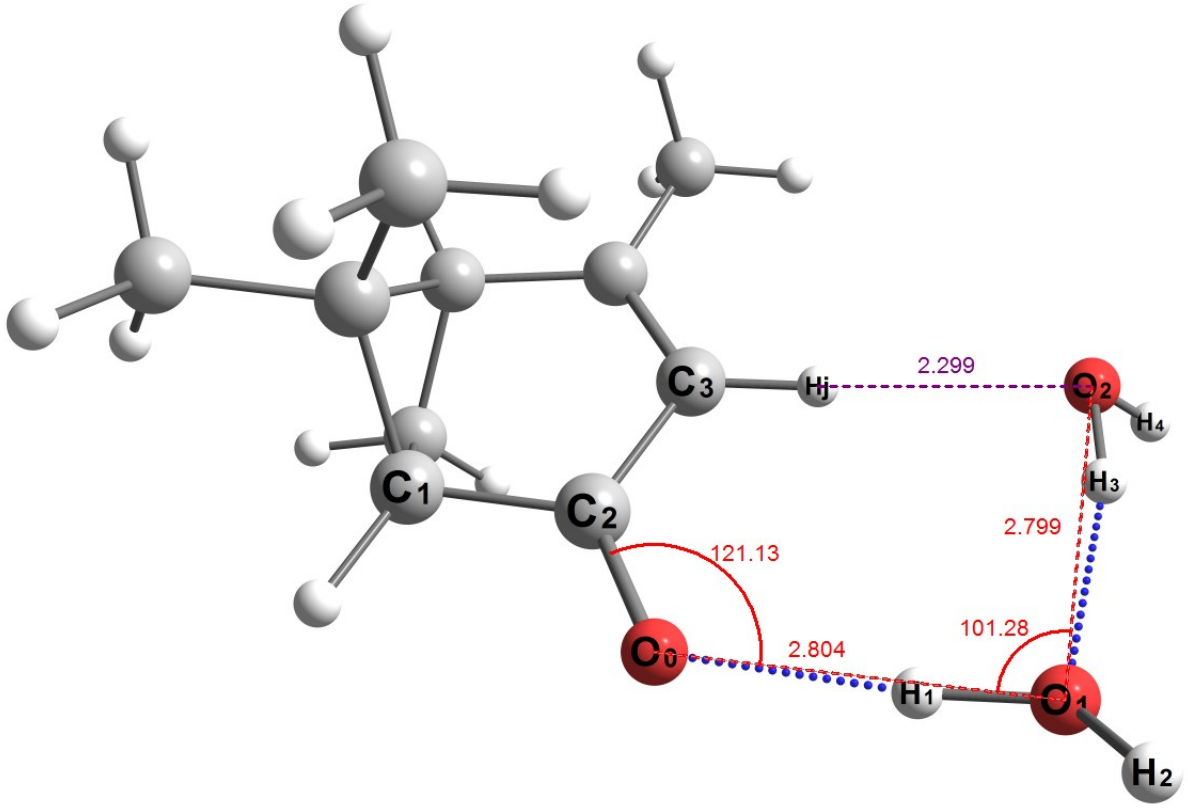
Table S16: Measured frequencies ($\nu_{\text{obs.}}$) and residuals ($\nu_{\text{obs.}} - \nu_{\text{calc.}}$) in MHz of the dihydrate of verbenone 2w-I with the $^{16}O_2$ atom substituted by a ^{18}O atom.

J'	K'_a	K'_c	$\leftarrow$	J''	K''_a	K''_c	$\nu_{\text{obs.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	exp. error
					$^aR_{0,1}$ transitions				
5	1	5	$\leftarrow$	4	1	4	4489.1463	0.0023	0.002
5	1	4	$\leftarrow$	4	1	3	4992.7692	0.0000	0.001
5	2	3	$\leftarrow$	4	2	2	5013.7555	−0.0004	0.001
6	0	6	$\leftarrow$	5	0	5	5414.8099	−0.0002	0.001
6	1	6	$\leftarrow$	5	1	5	5362.3365	0.0007	0.001
6	1	5	$\leftarrow$	5	1	4	5930.3025	0.0005	0.001
6	2	5	$\leftarrow$	5	2	4	5702.8039	0.0003	0.001
6	2	4	$\leftarrow$	5	2	3	6054.4834	0.0000	0.001
7	0	7	$\leftarrow$	6	0	6	6259.9958	−0.0004	0.001
7	1	7	$\leftarrow$	6	1	6	6228.9578	0.0000	0.001
7	1	6	$\leftarrow$	6	1	5	6830.6899	0.0006	0.001
7	2	6	$\leftarrow$	6	2	5	6617.7505	0.0000	0.001
7	2	5	$\leftarrow$	6	2	4	7077.8373	0.0001	0.001
7	3	4	$\leftarrow$	6	3	3	6930.6705	−0.0004	0.002
8	0	8	$\leftarrow$	7	0	7	7108.0055	0.0000	0.001
8	1	8	$\leftarrow$	7	1	7	7090.9518	0.0001	0.001
8	1	7	$\leftarrow$	7	1	6	7695.8755	−0.0002	0.001
8	2	7	$\leftarrow$	7	2	6	7519.3706	−0.0001	0.001
8	2	6	$\leftarrow$	7	2	5	8074.0296	−0.0001	0.002
8	3	5	$\leftarrow$	7	3	4	7992.3391	−0.0001	0.002
9	0	9	$\leftarrow$	8	0	8	7958.8991	−0.0003	0.002
9	1	9	$\leftarrow$	8	1	8	7949.9845	−0.0002	0.002
9	1	8	$\leftarrow$	8	1	7	8538.0238	−0.0016	0.002
9	2	8	$\leftarrow$	8	2	7	8408.5230	−0.0015	0.002

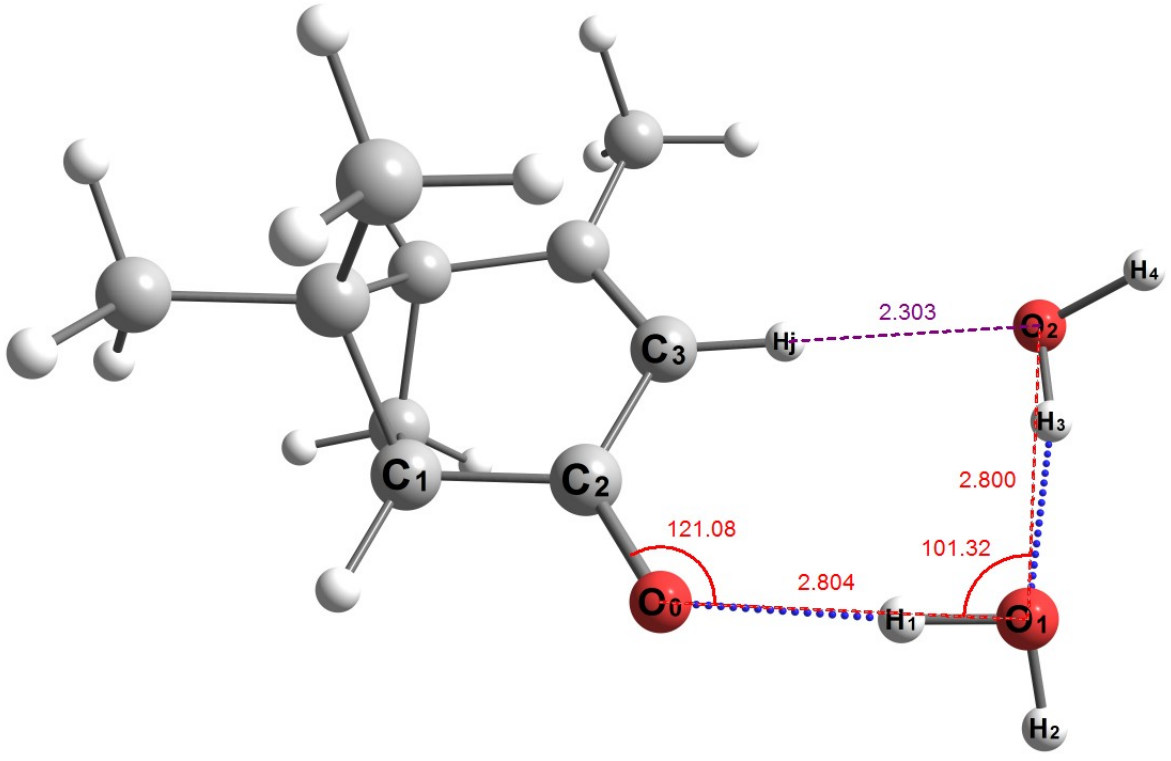
Table S17: Measured frequencies ($\nu_{\text{obs.}}$) and residuals ($\nu_{\text{obs.}} - \nu_{\text{calc.}}$) in MHz of the dihydrate of verbenone 2w-I with the $^{16}O_1$ and $^{16}O_2$ atoms substituted by ^{18}O atoms.

J'	K'_a	K'_c	$\leftarrow$	J''	K''_a	K''_c	$\nu_{\text{obs.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	exp. error
					$^aR_{0,1}$ transitions				
4	0	4	$\leftarrow$	3	0	3	3627.2897	−0.0012	0.001
4	1	4	$\leftarrow$	3	1	3	3524.4825	0.0004	0.001
4	1	3	$\leftarrow$	3	1	2	3929.5120	0.0000	0.001
4	2	3	$\leftarrow$	3	2	2	3744.6661	0.0068	0.005
5	0	5	$\leftarrow$	4	0	4	4466.9648	−0.0007	0.001
5	1	5	$\leftarrow$	4	1	4	4386.2602	−0.0005	0.002
5	1	4	$\leftarrow$	4	1	3	4876.6969	−0.0004	0.001
5	2	4	$\leftarrow$	4	2	3	4663.1503	0.0006	0.001
5	2	3	$\leftarrow$	4	2	2	4890.1987	0.0009	0.001
6	0	6	$\leftarrow$	5	0	5	5294.3080	−0.0006	0.002
6	1	6	$\leftarrow$	5	1	5	5239.9870	0.0000	0.002
6	1	5	$\leftarrow$	5	1	4	5795.1727	−0.0004	0.002
6	2	5	$\leftarrow$	5	2	4	5570.4637	0.0006	0.001
6	2	4	$\leftarrow$	5	2	3	5906.6563	−0.0026	0.002
7	0	7	$\leftarrow$	6	0	6	6120.0095	−0.0007	0.002
7	1	7	$\leftarrow$	6	1	6	6087.2667	−0.0004	0.001
7	1	6	$\leftarrow$	6	1	5	6678.5281	0.0005	0.001
7	2	6	$\leftarrow$	6	2	5	6465.3801	0.0009	0.001
7	2	5	$\leftarrow$	6	2	4	6907.6975	−0.0004	0.001
7	3	5	$\leftarrow$	6	3	4	6628.0592	0.0005	0.001
7	3	4	$\leftarrow$	6	3	3	6758.1434	−0.0008	0.001
7	4	4	$\leftarrow$	6	4	3	6639.5468	0.0043	0.005
7	4	3	$\leftarrow$	6	4	2	6649.7932	−0.0045	0.005
8	0	8	$\leftarrow$	7	0	7	6948.2442	−0.0002	0.001
8	1	8	$\leftarrow$	7	1	7	6929.9277	0.0000	0.001
8	1	7	$\leftarrow$	7	1	6	7527.5185	0.0008	0.001
8	2	7	$\leftarrow$	7	2	6	7347.5649	0.0002	0.001
8	2	6	$\leftarrow$	7	2	5	7883.7132	0.0001	0.001

J'	K'_a	K'_c	$\leftarrow$	J''	K''_a	K''_c	$\nu_{\text{obs.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	exp. error
8	3	6	$\leftarrow$	7	3	5	7566.1961	0.0000	0.001
8	3	5	$\leftarrow$	7	3	4	7792.1107	−0.0006	0.001
8	4	5	$\leftarrow$	7	4	4	7600.7272	0.0009	0.002
8	4	4	$\leftarrow$	7	4	3	7627.8158	−0.0007	0.001
9	0	9	$\leftarrow$	8	0	8	7779.3182	−0.0003	0.001
9	1	9	$\leftarrow$	8	1	8	7769.5773	0.0001	0.001
9	1	8	$\leftarrow$	8	1	7	8352.6042	0.0004	0.002
9	2	8	$\leftarrow$	8	2	7	8217.7009	0.0003	0.002
9	3	7	$\leftarrow$	8	3	6	8493.5214	0.0004	0.002
9	4	6	$\leftarrow$	8	4	5	8562.4234	0.0002	0.002
10	0	10	$\leftarrow$	9	0	9	8612.4127	−0.0007	0.002
10	1	10	$\leftarrow$	9	1	9	8607.4133	−0.0006	0.002
							$^{b}R_{-1,-1}$		
7	0	7	$\leftarrow$	6	1	6	6049.3682	0.0000	0.001
8	0	8	$\leftarrow$	7	1	7	6910.3455	0.0000	0.001
8	1	7	$\leftarrow$	7	2	6	6993.4085	0.0015	0.002
9	0	9	$\leftarrow$	8	1	8	7759.7362	−0.0002	0.001
9	1	8	$\leftarrow$	8	2	7	7998.4476	0.0016	0.002
							$^{b}R_{1,1}$		
4	4	1	$\leftarrow$	3	3	0	7654.1189	0.0003	0.002
4	4	0	$\leftarrow$	3	3	1	7655.4492	−0.0005	0.002
7	1	7	$\leftarrow$	6	0	6	6157.9094	0.0002	0.001
8	1	8	$\leftarrow$	7	0	7	6967.8265	0.0000	0.002
9	1	9	$\leftarrow$	8	0	8	7789.1594	0.0001	0.002



(a) 2w-II(a)



(b) 2w-II(b) ($+0.22\,\mathrm{kJ\,mol^{-1}}$)

Figure S4: Two optimized (MP2/6-311++G(d,p)) close structures of the highest energy conformer 2w-II, differing by the orientation of the water molecules. Lengths expressed in Å, angles in °.

Table S18: Experimental rotational constants of the observed conformer of the dihydrate of verbenone 2w-II, and comparison with the sets of computed constants corresponding to the two possible structures 2w-II(a) and 2w-II(b) represented Fig. S4.

		2w-II(a)				2w-II (b)			
	Exp.	MP2 [a]	Dev.[b]	DFT [c]	Dev.[b]	MP2 [a]	Dev. [b]	DFT [c]	Dev. [b]
A/MHz	1063.5954(14)	1070.50	0.65	1071.82	0.77	1077.08	1.27	1081.07	1.64
B/MHz	473.579785(93)	471.32	-0.48	481.30	1.63	468.32	-1.11	475.71	0.45
C/MHz	395.166703(58)	391.87	-0.83	401.60	1.63	389.51	-1.43	396.95	0.45
N_{lines}	68								
κ [d]	-0.765	-0.765		-0.762		-0.771		-0.770	
$P_a(u.\text{Å}^2)$	935.4432(4)	944.91		918.46		953.70		934.02	
$P_b(u.\text{Å}^2)$	343.4576(4)	344.75		339.95		343.78		339.13	
$P_c(u.\text{Å}^2)$	131.7033(4)5	127.35		131.57		125.44		128.35	
$\mid \mu_a \mid$/D		3.18		3.77		3.16		3.86	
$\mid \mu_b \mid$/D		0.78		1.12		0.78		1.11	
$\mid \mu_c \mid$/D		0.07		0.17		0.23		0.17	
ΔE [e] / (kJ mol^{-1})		0.0		0.0		0.19		0.22	

[a] MP2 / 6-311++G(d,p) ; [b] Deviation (%) calculated as (calc. − exp.)/exp. ; [c] B3LYP-D3BJ / def2-TZVP ; [d] $\kappa = (2B - A - C)/(A - C)$; [e] difference of energy, including ZPE correction, with respect to the lowest energy conformer 2w-II (a).

Table S19: Experimental rotational and quartic centrifugal distortion constants of the normal and of the $H_2^{18}O$ substituted species of the complex of verbenone 2w-II.

	Normal	$^{18}O_1$-$^{18}O_2$	$^{18}O_1$-$^{16}O_2$	$^{16}O_1$-$^{18}O_2$
A (MHz)	1063.5954(14)	1045.5043(10)	1053.9684(35)	1055.9401(29)
B (MHz)	473.579 785(93)	449.475 942(36)	461.878 251(70)	460.146 792(66)
C (MHz)	395.166 703(58)	376.067 902(34)	385.726 504(61)	384.886 165(44)
Δ_J (kHz)	0.082 89(31)	0.078 16(16)	[b]	[b]
Δ_{JK} (kHz)	0.1051(26)	[b]	[b]	[b]
Δ_K (kHz)	-	-	-	-
δ_J(kHz)	0.005 50(22)	[b]	[b]	[b]
δ_K(kHz)	0.1095(32)	[b]	[b]	[b]
N_{lines} [a]	49	40	18	25
σ_{fit} (kHz)	0.81	0.69	0.86	0.88
$P_a(u.\text{Å}^2)$	935.4432(4)	992.4206(3)	962.4408(8)	966.3774(7)
$P_b(u.\text{Å}^2)$	343.4576(4)	351.4298(3)	347.7596(8)	346.6836(7)
$P_c(u.\text{Å}^2)$	131.7033(4)	131.9532(3)	131.7415(8)	131.9222(7)

[a] The number of fitted lines ; [b] Fixed at the value of the normal species.

Table S20: Experimental coordinates (in Å, in the principal axes systems) of the water oxygen atoms in the observed conformer of the dihydrate of verbenone 2w-II, along with those obtained by *ab initio* and DFT calculations for the conformer 2w-II(a).

	a	*b*	*c*
		O_1	
r_s/ Å	3.6764(4)	1.5060(10)	−0.143(11)
r_0/ Å	3.691(5)	1.492(1)	−0.143(1)
MP2 [a] / Å	3.772	1.487	−0.158
DFT [b] / Å	3.693	1.483	−0.170
		O_2	
r_s/ Å	3.938 44(38)	−1.3077(12)	−0.3411(44)
r_0/ Å	3.950(4)	−1.291(2)	−0.387(1)
MP2 [a] / Å	3.915	−1.305	−0.298
DFT [b] / Å	3.863	−1.287	−0.368

[a] MP2 / 6-311++G(d,p) ; [b] B3LYP-D3BJ / def2-TZVP .

Table S21: The substitution and effective structural parameters of the observed verbenone dihydrate 2w-II, along with those optimized by quantum chemistry for the conformer 2w-II(a).

Parameters [a]	r_s	r_0 [b]	B3LYP [c]	MP2 [d]
$r(O_1O_0)$/ Å	-	2.7466(44)	2.759	2.804
$r(O_2O_1)$/ Å	2.833(3)	2.8050(14)	2.782	2.799
$\angle(O_1O_0C_2)$ [e] / °	-	121.13(4)	119.8	121.1
$\angle(O_2O_1O_0)$/ °	-	104.50(17)	102.6	101.3
$\tau(O_1O_0C_2C_1)$/ °	-	5.207(45)	5.0	5.0
σ_{fit}/u$Å^2$	-	0.127	-	-

[a] Numbering scheme is shown Fig. S4a ; [b] Parameters involving the H atoms taken from the MP2/6-311++G(d,p) optimized geometry of conformer 2w-II(a) ; [c] B3LYP-D3BJ / def2-TZVP ; [d] MP2/6-311++G(d,p) ; [e] not fitted, calculated from the output coordinates.

Table S22: Experimental coordinates (in Å, in the principal axes systems) of the water oxygen atoms in the observed dihydrate of verbenone 2w-II, compared with those obtained by *ab initio* and DFT calculations for the conformer 2w-II(b).

	a	*b*	*c*
		O_1	
r_s/ Å	3.6764(4)	1.5060(10)	−0.143(11)
r_0/ Å	3.680(54)	1.495(5)	−0.109(15)
MP2 [a] / Å	3.802	1.470	−0.109
DFT [b] / Å	3.742	1.465	−0.130
		O_2	
r_s/ Å	3.938 44(38)	−1.3077(12)	−0.3411(44)
r_0/ Å	3.934(5)	−1.317(13)	−0.429(23)
MP2 [a] / Å	3.920	−1.321	−0.295
DFT [b] / Å	3.887	−1.305	−0.330

[a] MP2 / 6-311++G(d,p) ; [b] B3LYP-D3BJ / def2-TZVP.

Table S23: The substitution and effective structural parameters of the observed verbenone dihydrate 2w-II, along with those optimized by quantum chemistry for the conformer 2w-II(b).

Parameters [a]	r_s	r_0 [b]	B3LYP [c]	MP2 [d]
$r(O_1O_0)$/ Å	-	2.733(65)	2.760	2.804
$r(O_2O_1)$/ Å	2.833(2)	2.842(14)	2.781	2.800
$\angle(O_1O_0C_2)$/ °	-	120.4(27)	120.4	121.1
$\angle(O_2O_1O_0)$/ °	-	105.07(85)	102.3	101.3
$\tau(H_4O_2H_3O_1)$/ °	-	157(20)	104.0	126.2
σ_{fit}/uÅ^2	-	0.086	-	-

[a] The numbering scheme is shown Fig. S4b ; [b] Parameters involving the H atoms taken from the MP2/6-311++G(d,p) optimized geometry of conformer 2w-II(b) ; [c] B3LYP-D3BJ / def2-TZVP ; [d] MP2/6-311++G(d,p).

Table S24: Measured frequencies ($\nu_{\text{obs.}}$) and residuals ($\nu_{\text{obs.}} - \nu_{\text{calc.}}$) in MHz of the dihydrate of verbenone 2w-II.

J'	K'_a	K'_c	$\leftarrow$	J''	K''_a	K''_c	$\nu_{\text{obs.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	exp. error
					$^aR_{0,1}$ transitions				
4	0	4	$\leftarrow$	3	0	3	3405.4152	−0.0025	0.001
4	1	4	$\leftarrow$	3	1	3	3304.7219	0.0000	0.001
4	1	3	$\leftarrow$	3	1	2	3615.8183	−0.0005	0.001
4	2	3	$\leftarrow$	3	2	2	3469.2668	0.0012	0.002
5	0	5	$\leftarrow$	4	0	4	4213.4589	0.0003	0.001
5	1	5	$\leftarrow$	4	1	4	4119.8503	0.0011	0.001
5	1	4	$\leftarrow$	4	1	3	4503.0825	0.0001	0.001
5	2	4	$\leftarrow$	4	2	3	4327.4606	0.0005	0.001
6	0	6	$\leftarrow$	5	0	5	5006.0682	−0.0004	0.002
6	1	6	$\leftarrow$	5	1	5	4929.5258	−0.0009	0.002
6	1	5	$\leftarrow$	5	1	4	5376.9810	0.0000	0.001
6	2	5	$\leftarrow$	5	2	4	5179.7185	0.0003	0.001
6	2	4	$\leftarrow$	5	2	3	5385.3162	−0.0007	0.001
6	3	4	$\leftarrow$	5	3	3	5241.7035	0.0016	0.002
6	3	3	$\leftarrow$	5	3	2	5264.7078	0.0002	0.001
7	0	7	$\leftarrow$	6	0	6	5790.5070	0.0005	0.002
7	1	7	$\leftarrow$	6	1	6	5734.1772	0.0012	0.001
7	1	6	$\leftarrow$	6	1	5	6233.2210	0.0001	0.001
7	2	6	$\leftarrow$	6	2	5	6025.1070	0.0002	0.001
7	2	5	$\leftarrow$	6	2	4	6313.2732	0.0005	0.002
7	3	5	$\leftarrow$	6	3	4	6118.2958	0.0000	0.001
7	3	4	$\leftarrow$	6	3	3	6168.0767	−0.0008	0.001
7	4	4	$\leftarrow$	6	4	3	6116.5468	0.0021	0.001
7	4	3	$\leftarrow$	6	4	2	6118.9827	−0.0009	0.001
8	0	8	$\leftarrow$	7	0	7	6572.8144	0.0016	0.002
8	1	8	$\leftarrow$	7	1	7	6534.5690	0.0009	0.002
8	1	7	$\leftarrow$	7	1	6	7068.1195	0.0003	0.001
8	2	7	$\leftarrow$	7	2	6	6862.9479	−0.0001	0.002
8	2	6	$\leftarrow$	7	2	5	7233.3429	0.0006	0.001

J'	K'_a	K'_c	$\leftarrow$	J''	K''_a	K''_c	$\nu_{\text{obs.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	exp. error
7	3	5	$\leftarrow$	6	3	4	6118.2958	0.0000	0.001
7	3	4	$\leftarrow$	6	3	3	6168.0767	−0.0008	0.001
7	4	4	$\leftarrow$	6	4	3	6116.5468	0.0021	0.001
7	4	3	$\leftarrow$	6	4	2	6118.9827	−0.0009	0.001
8	0	8	$\leftarrow$	7	0	7	6572.8144	0.0016	0.002
8	1	8	$\leftarrow$	7	1	7	6534.5690	0.0009	0.002
8	1	7	$\leftarrow$	7	1	6	7068.1195	0.0003	0.001
8	2	7	$\leftarrow$	7	2	6	6862.9479	−0.0001	0.002
8	2	6	$\leftarrow$	7	2	5	7233.3429	0.0006	0.001
8	3	6	$\leftarrow$	7	3	5	6992.7202	−0.0002	0.001
8	3	5	$\leftarrow$	7	3	4	7086.2538	−0.0002	0.001
8	4	5	$\leftarrow$	7	4	4	6998.4668	0.0005	0.001
8	4	4	$\leftarrow$	7	4	3	7005.0573	−0.0011	0.001
9	0	9	$\leftarrow$	8	0	8	7356.1053	−0.0003	0.001
9	1	9	$\leftarrow$	8	1	8	7331.6222	−0.0001	0.001
9	1	8	$\leftarrow$	8	1	7	7880.4845	−0.0004	0.001
9	2	8	$\leftarrow$	8	2	7	7692.9109	−0.0021	0.001
9	2	7	$\leftarrow$	8	2	6	8139.8538	0.0009	0.001
10	0	10	$\leftarrow$	9	0	9	8141.2544	−0.0003	0.001
10	1	10	$\leftarrow$	9	1	9	8126.2298	−0.0007	0.001
11	0	11	$\leftarrow$	10	0	10	8928.0858	0.0000	0.001
11	1	11	$\leftarrow$	10	1	10	8919.1499	0.0025	0.002
12	0	12	$\leftarrow$	11	0	11	9716.1441	−0.0009	0.002
12	1	12	$\leftarrow$	11	1	11	9710.9510	0.0010	0.002
13	1	13	$\leftarrow$	12	1	12	10 502.0475	0.0011	0.002
							$^bR_{1,1}$ transitions		
8	1	8	$\leftarrow$	7	0	7	6633.1264	0.0005	0.002
9	1	9	$\leftarrow$	8	0	8	7391.9367	0.0012	0.002
							$^bR_{-1,1}$ transitions		
8	0	8	$\leftarrow$	7	1	7	6474.2531	−0.0018	0.002
9	0	9	$\leftarrow$	8	1	8	7295.7935	0.0009	0.002

Table S25: Measured frequencies ($\nu_{\text{obs.}}$) and residuals ($\nu_{\text{obs.}} - \nu_{\text{calc.}}$) in MHz of the dihydrate of verbenone 2w-II with the $^{16}O_1$ atom substituted by a ^{18}O atom.

J'	K'_a	K'_c	$\leftarrow$	J''	K''_a	K''_c	$\nu_{\text{obs.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	exp. error
					$^aR_{0,1}$ transitions				
6	0	6	$\leftarrow$	5	0	5	4889.1997	0.0000	0.002
6	1	6	$\leftarrow$	5	1	5	4811.9534	−0.0023	0.001
6	1	5	$\leftarrow$	5	1	4	5247.7859	−0.0003	0.002
6	2	4	$\leftarrow$	5	2	3	5250.4571	0.0000	0.002
7	0	7	$\leftarrow$	6	0	6	5655.3905	0.0000	0.001
7	1	6	$\leftarrow$	6	1	5	6085.0631	−0.0019	0.002
7	1	7	$\leftarrow$	6	1	6	5597.7508	−0.0007	0.002
7	2	6	$\leftarrow$	6	2	5	5880.3197	−0.0027	0.002
7	2	5	$\leftarrow$	6	2	4	6155.8865	−0.0021	0.002
8	0	8	$\leftarrow$	7	0	7	6419.0691	0.0010	0.002
8	1	7	$\leftarrow$	7	1	6	6902.2220	0.0002	0.002
8	1	8	$\leftarrow$	7	1	7	6379.3910	0.0008	0.002
8	2	7	$\leftarrow$	7	2	6	6698.7273	−0.0008	0.002
8	2	6	$\leftarrow$	7	2	5	7054.4759	0.0011	0.001
8	3	5	$\leftarrow$	7	3	4	6908.2827	0.0000	0.002
9	0	9	$\leftarrow$	8	0	8	7183.4736	0.0014	0.002
9	1	9	$\leftarrow$	8	1	8	7157.7312	0.0010	0.001
9	2	8	$\leftarrow$	8	2	7	7509.6236	0.0012	0.002

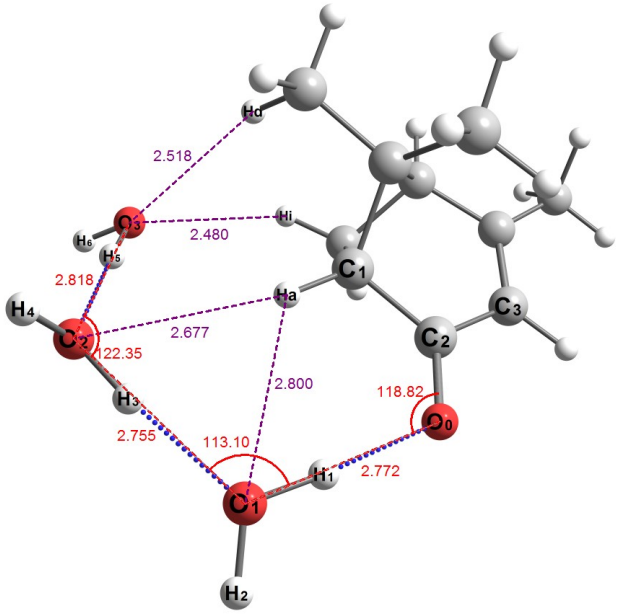
Table S26: Measured frequencies ($\nu_{\text{obs.}}$) and residuals ($\nu_{\text{obs.}} - \nu_{\text{calc.}}$) in MHz of the dihydrate of verbenone 2w-II with the $^{16}O_2$ atom substituted by a ^{18}O atom.

J'	K'_a	K'_c	$\leftarrow$	J''	K''_a	K''_c	$\nu_{\text{obs.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	exp. error
					$^aR_{0,1}$ transitions				
5	0	5	$\leftarrow$	4	0	4	4104.8044	0.0005	0.002
5	1	4	$\leftarrow$	4	1	3	4379.9363	−0.0013	0.002
6	0	6	$\leftarrow$	5	0	5	4878.2554	−0.0020	0.002
6	1	6	$\leftarrow$	5	1	5	4800.3265	−0.0018	0.001
6	1	5	$\leftarrow$	5	1	4	5231.7250	−0.0002	0.001
6	2	5	$\leftarrow$	5	2	4	5040.1855	−0.0021	0.002
6	2	4	$\leftarrow$	5	2	3	5231.4399	−0.0005	0.002
7	0	7	$\leftarrow$	6	0	6	5643.1016	−0.0011	0.002
7	1	7	$\leftarrow$	6	1	6	5584.5136	−0.0013	0.001
7	1	6	$\leftarrow$	6	1	5	6067.5166	0.0000	0.001
7	2	6	$\leftarrow$	6	2	5	5863.7845	−0.0008	0.002
7	2	5	$\leftarrow$	6	2	4	6133.7678	0.0012	0.002
8	0	8	$\leftarrow$	7	0	7	6405.2180	−0.0005	0.001
8	1	8	$\leftarrow$	7	1	7	6364.5818	−0.0007	0.002
8	1	7	$\leftarrow$	7	1	6	6883.7515	−0.0011	0.002
8	2	7	$\leftarrow$	7	2	6	6680.3966	−0.0005	0.002
8	2	6	$\leftarrow$	7	2	5	7029.7702	0.0030	0.002
9	0	9	$\leftarrow$	8	0	8	7167.9177	0.0005	0.001
9	1	9	$\leftarrow$	8	1	8	7141.3612	0.0003	0.001
9	1	8	$\leftarrow$	8	1	7	7678.8007	0.0011	0.002
9	2	8	$\leftarrow$	8	2	7	7489.6620	0.0008	0.002
10	0	10	$\leftarrow$	9	0	9	7932.3043	0.0021	0.001

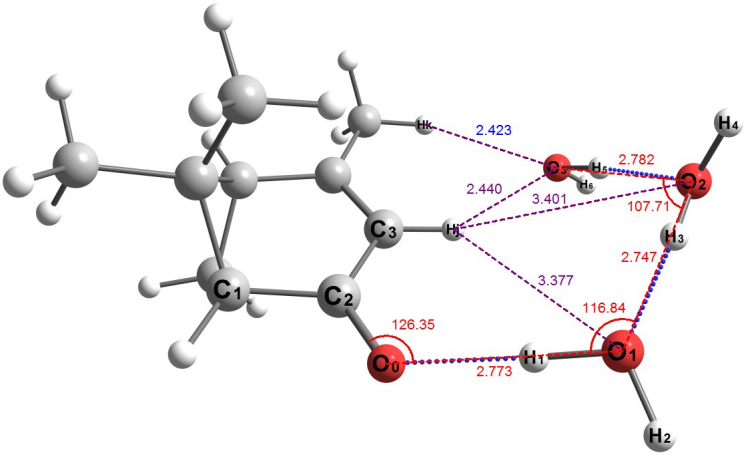
Table S27: Measured frequencies ($\nu_{\text{obs.}}$) and residuals ($\nu_{\text{obs.}} - \nu_{\text{calc.}}$) in MHz of the dihydrate of verbenone 2w-II with the $^{16}O_1$ and $^{16}O_2$ atoms substituted by ^{18}O atoms.

J'	K'_a	K'_c	←	J''	K''_a	K''_c	$\nu_{\text{obs.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	exp. error
					$^aR_{0,1}$ transitions				
4	1	4	←	3	1	3	3143.5727	−0.0014	0.001
5	0	5	←	4	0	4	4012.5680	0.0001	0.002
5	1	4	←	4	1	3	4279.5384	0.0001	0.001
5	1	5	←	4	1	4	3919.6845	0.0011	0.001
5	2	3	←	4	2	2	4228.5122	−0.0017	0.001
6	0	6	←	5	0	5	4769.0542	−0.0006	0.001
6	1	6	←	5	1	5	4690.8559	0.0001	0.001
6	2	5	←	5	2	4	4924.6712	0.0004	0.001
7	0	7	←	6	0	6	5516.7892	0.0009	0.001
7	1	7	←	6	1	6	5457.3817	0.0002	0.001
7	1	6	←	6	1	5	5930.3403	0.0010	0.001
7	2	5	←	6	2	4	5989.8379	−0.0001	0.002
7	2	6	←	6	2	5	5729.7745	0.0000	0.001
7	3	4	←	6	3	3	5853.1678	−0.0006	0.001
8	0	8	←	7	0	7	6261.5172	−0.0002	0.001
8	1	8	←	7	1	7	6219.8785	0.0002	0.001
8	1	7	←	7	1	6	6729.5474	0.0003	0.001
8	2	7	←	7	2	6	6528.1891	−0.0006	0.001
8	2	6	←	7	2	5	6865.8570	0.0014	0.002
8	3	5	←	7	3	4	6721.1743	−0.0001	0.002
9	0	9	←	8	0	8	7006.6201	0.0005	0.002
9	1	8	←	8	1	7	7508.3465	−0.0004	0.001
9	1	9	←	8	1	8	6979.1297	0.0004	0.002
9	2	8	←	8	2	7	7319.5437	−0.0006	0.001
9	2	8	←	8	2	7	7319.5441	−0.0002	0.001
9	2	7	←	8	2	6	7730.8339	0.0009	0.001
9	3	7	←	8	3	6	7472.0294	−0.0007	0.002
9	3	6	←	8	3	5	7603.0063	0.0016	0.002
9	4	6	←	8	4	5	7486.0286	0.0007	0.002

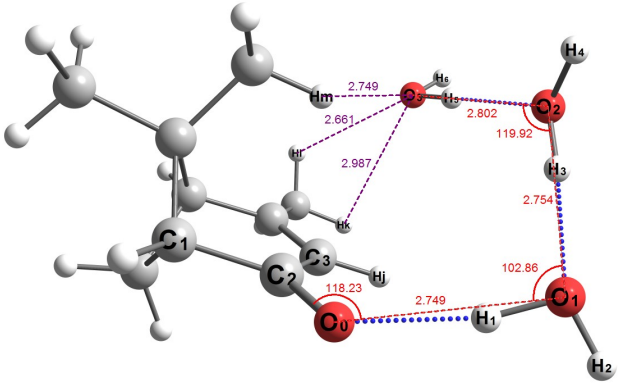
J'	K'_a	K'_c	$\leftarrow$	J''	K''_a	K''_c	$\nu_{\text{obs.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	exp. error
10	0	10	$\leftarrow$	9	0	9	7753.3056	−0.0005	0.002
10	1	10	$\leftarrow$	9	1	9	7735.9310	0.0004	0.002
12	0	12	$\leftarrow$	11	0	11	9251.2104	0.0014	0.002
12	1	11	$\leftarrow$	11	1	10	9752.7856	−0.0025	0.002
12	1	12	$\leftarrow$	11	1	11	9244.8545	0.0020	0.002
12	2	11	$\leftarrow$	11	2	10	9652.6489	−0.0019	0.002
							$^{b}R_{-1,1}$		
7	0	7	$\leftarrow$	6	1	6	5345.2057	−0.0015	0.002
8	0	8	$\leftarrow$	7	1	7	6149.3421	−0.0011	0.002
9	0	9	$\leftarrow$	8	1	8	6936.0855	0.0009	0.002
							$^{b}R_{1,1}$		
8	1	8	$\leftarrow$	7	0	7	6332.0536	0.0011	0.002
9	1	9	$\leftarrow$	8	0	8	7049.6634	−0.0008	0.002



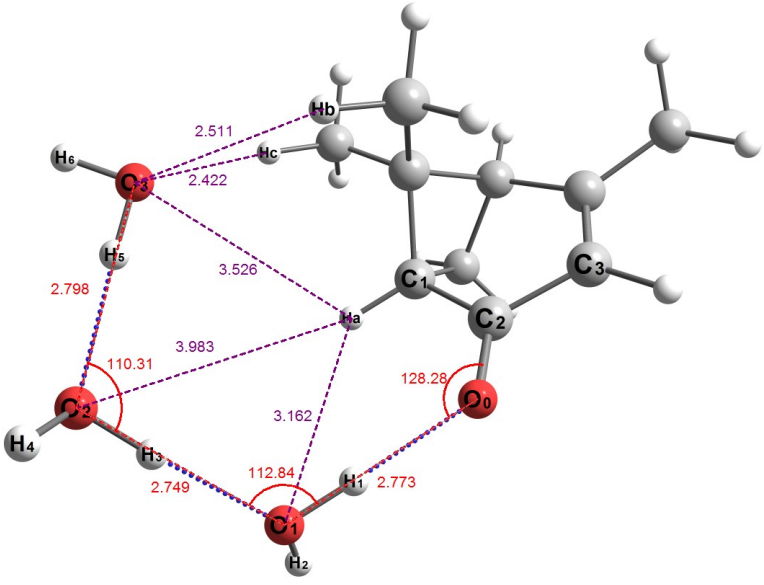
(a) 3w-I, $\tau(O_0O_1O_2O_3) = 5.4°$



(b) 3w-II (+2.80 kJ mol^{-1}), $\tau(O_0O_1O_2O_3) = -27.3°$



(c) 3w-III (+4.06 kJ mol^{-1}), $\tau(O_0O_1O_2O_3) = -47.3°$



(d) 3w-IV (+5.67 kJ mol^{-1}), $\tau(O_0O_1O_2O_3) = 29.5°$

Figure S5: The 4 optimized structures of the trihydrate of verbenone calculated at the MP2 / 6-311++G(d,p) level using Gaussian 16. Energies (including ZPE corrections) shown into parentheses are energies relative to the lowest energy conformer 3w-I. The pictures show how the terminal oxygen atom O_3 of the chain of water molecules is anchored to verbenone by Van der Waals interactions, with lengths expressed in Å and angles in °. The dihedral angle $\tau(O_0O_1O_2O_3)$ of the four atoms of oxygen is given for each conformer.

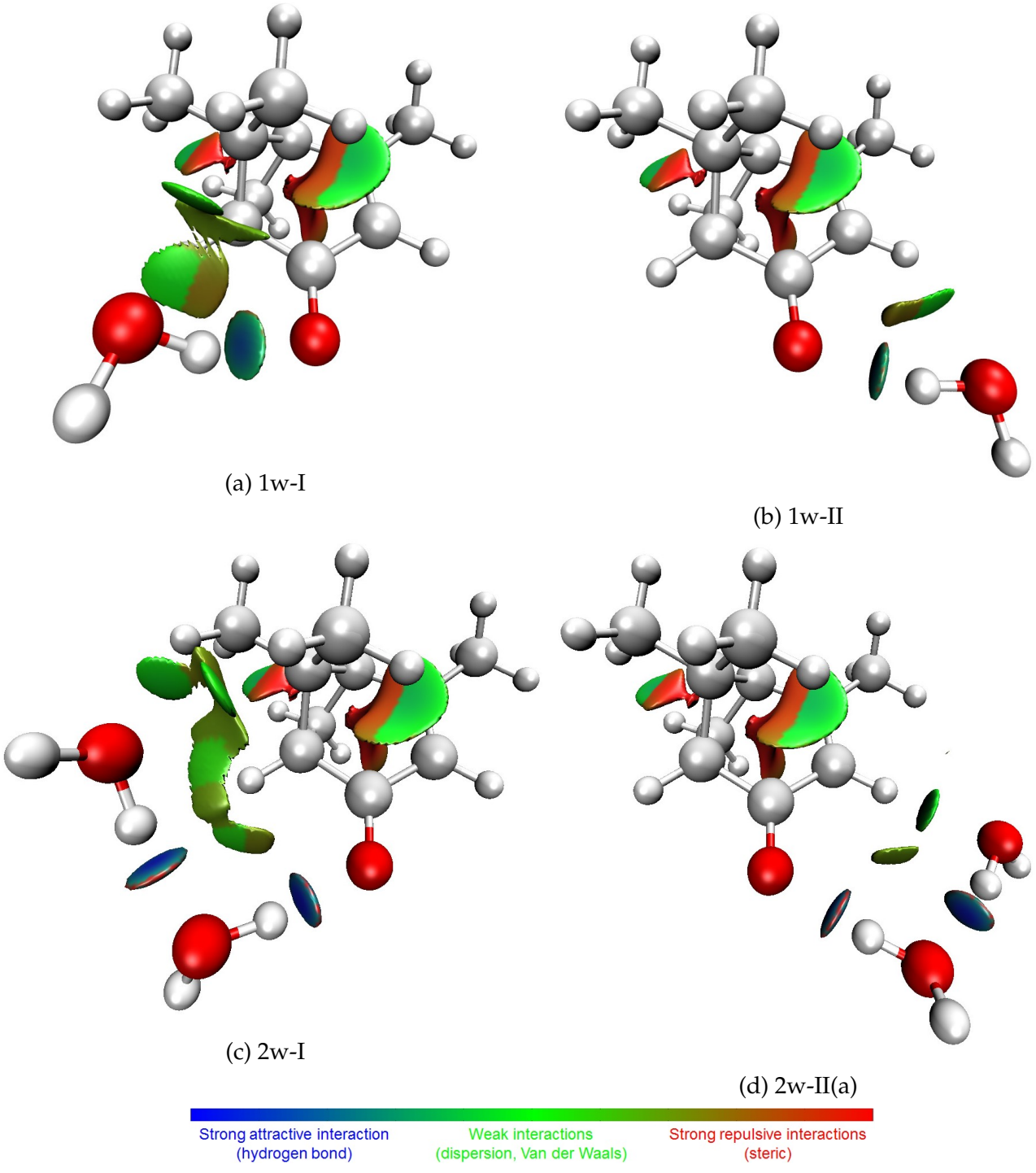
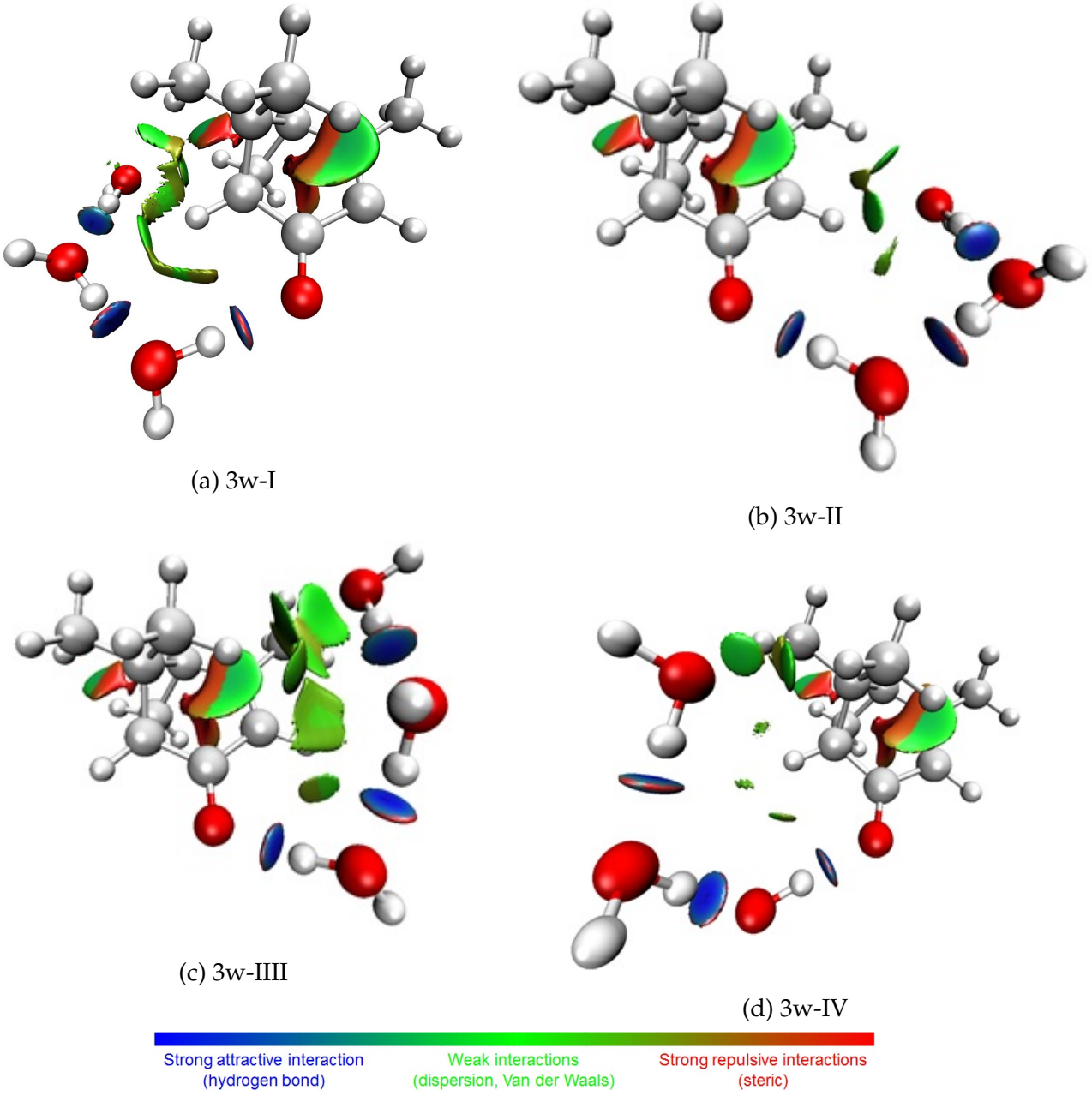


Figure S6: NCI plots showing the interactions in the mono and dihydrates of verbenone.



(a) 3w-I

(b) 3w-II

(c) 3w-IIII

(d) 3w-IV

Figure S7: NCI plots showing the interactions in the trihydrates of verbenone.

Table S28: Calculated rotational constants, dipole moments and relative energies (including ZPE corrections) of the 4 trihydrates of verbenone shown Figure S5.

Parameter	DFT [a]	MP2 [b]	DFT [a]	MP2 [b]
	3w-I		3w-II	
A / MHz	786.83	789.22	839.54	822.11
B / MHz	432.56	428.49	368.65	368.55
C / MHz	347.74	345.81	303.93	304.99
$\mid \mu_a \mid$ / D	2.31	1.66	3.00	2.41
$\mid \mu_b \mid$ / D	0.55	0.32	0.75	0.42
$\mid \mu_c \mid$ / D	0.25	0.05	0.48	0.19
ΔE [c] / kJ mol^{-1}	-	-	1.28	2.80
	3w-III		3w-IV	
A / MHz	690.57	723.27	842.35	833.94
B / MHz	493.40	451.21	390.93	380.90
C / MHz	404.68	383.96	315.63	307.77
$\mid \mu_a \mid$ / D	1.31	1.67	3.46	3.00
$\mid \mu_b \mid$ / D	0.73	0.60	0.51	0.26
$\mid \mu_c \mid$ / D	1.20	0.67	1.41	1.19
ΔE [c] / kJ mol^{-1}	1.74	4.06	4.36	5.67

[a] B3LYP-D3BJ/def2TZVP ; [b] MP2 / 6-311++G(d,p) ; [c] Energy gap relative to conformer 3w-I (including ZPE correction).

Table S29: Experimental rotational and quartic centrifugal distortion constants of the normal and of the $H_2^{18}O$ substituted species of the trihydrate of verbenone 3w-I.

	Normal	$^{18}O_1$-$^{18}O_2$-$^{18}O_3$	$^{18}O_1$-$^{18}O_2$-$^{16}O_3$	$^{18}O_1$-$^{16}O_2$-$^{18}O_3$
A (MHz)	786.574 06(35)	757.324 99(47)	773.0744(18)	757.6496(24)
B (MHz)	422.802 573(55)	401.930 189(31)	407.005 360(78)	411.544 25(12)
C (MHz)	342.662 068(35)	324.836 651(28)	329.858 360(48)	331.067 339(51)
Δ_J (kHz)	0.047 53(15)	0.044 92(15)	[c]	[c]
Δ_{JK} (kHz)	0.1414(15)	[b]	[b]	[b]
Δ_K (kHz)	-	-	-	-
δ_J (kHz)	0.004 51(12)	[b]	[b]	[b]
δ_K (kHz)	-	-	-	-
N_{lines} [a]	66	45	20	20
σ_{fit} (kHz)	0.91	1.01	1.41	0.93
$P_a(u.\text{Å}^2)$	1013.8310(2)	1072.9266(3)	1060.0420(8)	1043.7427(10)
$P_b(u.\text{Å}^2)$	461.0303(2)	482.8677(3)	472.0671(8)	482.7715(10)
$P_c(u.\text{Å}^2)$	181.4763(2)	184.4535(3)	181.6591(8)	184.2638(10)
	$^{16}O_1$-$^{18}O_2$-$^{18}O_3$	$^{18}O_1$-$^{16}O_2$-$^{16}O_3$	$^{16}O_1$-$^{18}O_2$-$^{16}O_3$	$^{16}O_1$-$^{16}O_2$-$^{18}O_3$
A (MHz)	770.8859(13)	773.4845(19)	786.2821(18)	771.1516(26)
B (MHz)	406.908 981(55)	416.961 457(85)	412.392 651(56)	416.926 829(89)
C (MHz)	330.588 969(34)	336.382 225(39)	335.804 323(34)	337.134 294(51)
Δ_J (kHz)	[c]	[b]	[b]	[b]
Δ_{JK} (kHz)	[b]	[b]	[b]	[b]
Δ_K (kHz)	-	-	-	-
δ_J (kHz)	[b]	[b]	[b]	[b]
δ_K (kHz)	-	-	-	-
N_{lines} [a]	18	14	13	14
σ_{fit} (kHz)	0.89	0.90	0.79	1.59
$P_a(u.\text{Å}^2)$	1057.5681(6)	1030.5338(9)	1043.8578(8)	1027.9201(12)
$P_b(u.\text{Å}^2)$	471.1550(6)	471.8613(9)	461.1228(8)	471.1235(12)
$P_c(u.\text{Å}^2)$	184.4271(6)	181.5183(9)	181.6223(8)	184.2327(12)

[a] The number of fitted lines ; [b] fixed at the value of the normal species ; [c] fixed at the value of the totally substituted species.

Table S30: Experimental coordinates (in Å, in the principal axes systems) of the water oxygen atoms O_1, O_2 and O_3 of the verbenone trihydrate 3w-I, along with those obtained by *ab initio* and DFT calculations.

	a	*b*	*c*
		O_1	
r_s / Å	−2.8723(5)	−2.3709(6)	0.150(10)
r_0 / Å	−2.871(7)	−2.367(5)	0.214(5)
MP2 [a] / Å	−2.874	−2.349	0.224
DFT [b] / Å	−2.865	−2.342	0.215
		O_2	
r_s / Å	−3.8889(4)	0.222(7)	0.276(5)
r_0 / Å	−3.902(5)	0.193(4)	0.188(10)
MP2 [a] / Å	−3.895	0.208	0.138
DFT [b] / Å	−3.880	0.186	0.099
		O_3	
r_s / Å	−2.6355(6)	2.2724(7)	−1.210(1)
r_0 / Å	−2.643(8)	2.312(5)	−1.178(5)
MP2 [a] / Å	−2.551	2.326	−1.145
DFT [b] / Å	−2.559	2.328	−1.119

[a] MP2 / 6-311++G(d,p) ; [b] B3LYP-D3BJ / def2-TZVP.

Table S31: The substitution and effective structural parameters of the verbenone trihydrate 3w-I along with those optimized by quantum chemistry.

Parameters [a]	r_s	r_0 [b]	B3LYP [c]	MP2 [d]
$r(O_1O_0)$/ Å	-	2.7944(34)	2.723	2.772
$r(O_2O_1)$/ Å	2.7876(64)	2.760(11)	2.726	2.755
$r(O_3O_2)$/ Å	2.8256(58)	2.812(11)	2.797	2.818
$\angle(O_1O_0C_2)$ [e]/ °	-	118.83(18)	119.4	118.8
$\angle(O_2O_1O_0)$ [e]/ °	-	113.10(22)	113.4	113.1
$\angle(O_3O_2O_1)$ [e]/ °	119.30(18)	122.35(29)	123.6	122.4
$\tau(O_1O_0C_2C_1)$/ °	-	178.34(15)	176.8	178.3
$\tau(O_2O_1O_0C_2)$/ °	-	5.55(39)	2.9	6.6
$\tau(O_0O_1O_2O_3)$/ °	-	24.73(73)	21.6	20.9
σ_{fit}/uÅ^2	-	0.180	-	-

[a] The numbering scheme is shown Fig. S5a ; [b] Parameters involving the H atoms taken from the MP2/6-311++G(d,p) optimized geometry ; [c] B3LYP-D3BJ / def2-TZVP ; [d] MP2/6-311++G(d,p) ; [e] not fitted, calculated from the output coordinates.

Table S32: Measured frequencies ($\nu_{\text{obs.}}$) and residuals ($\nu_{\text{obs.}} - \nu_{\text{calc.}}$) in MHz of the trihydrate of verbenone 3w-I.

J'	K'_a	K'_c	$\leftarrow$	J''	K''_a	K''_c	$\nu_{\text{obs.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	exp. error
					$^aR_{0,1}$ transitions				
3	0	3	$\leftarrow$	2	0	2	2250.6443	0.0000	0.002
4	0	4	$\leftarrow$	3	0	3	2956.3061	0.0006	0.001
4	1	3	$\leftarrow$	3	1	2	3194.8542	−0.0007	0.001
4	1	4	$\leftarrow$	3	1	3	2880.8443	−0.0010	0.001
5	1	4	$\leftarrow$	4	1	3	3963.8140	0.0001	0.001
5	1	5	$\leftarrow$	4	1	4	3585.3233	−0.0002	0.001
5	2	4	$\leftarrow$	4	2	3	3801.0317	0.0009	0.001
6	0	6	$\leftarrow$	5	0	5	4320.4549	0.0000	0.001
6	1	5	$\leftarrow$	5	1	4	4708.5867	0.0005	0.001
6	1	6	$\leftarrow$	5	1	5	4283.4962	0.0000	0.001
6	2	4	$\leftarrow$	5	2	3	4809.5395	0.0000	0.001
6	2	5	$\leftarrow$	5	2	4	4540.2555	−0.0003	0.001
7	0	7	$\leftarrow$	6	0	6	4998.2089	0.0002	0.001
7	1	7	$\leftarrow$	6	1	6	4976.7744	0.0001	0.001
7	1	6	$\leftarrow$	6	1	5	5424.6408	0.0001	0.001
7	2	5	$\leftarrow$	6	2	4	5619.6004	0.0003	0.001
7	2	6	$\leftarrow$	6	2	5	5269.3649	0.0003	0.001
7	3	4	$\leftarrow$	6	3	3	5514.4088	−0.0003	0.001
7	3	5	$\leftarrow$	6	3	4	5401.6279	−0.0004	0.001
8	0	8	$\leftarrow$	7	0	7	5678.2234	−0.0002	0.001
8	1	8	$\leftarrow$	7	1	7	5666.6656	0.0000	0.001
8	1	7	$\leftarrow$	7	1	6	6114.4459	0.0001	0.001
8	2	7	$\leftarrow$	7	2	6	5988.2643	0.0000	0.001
8	2	6	$\leftarrow$	7	2	5	6408.0763	0.0002	0.001
8	3	5	$\leftarrow$	7	3	4	6356.7308	0.0011	0.001
8	3	6	$\leftarrow$	7	3	5	6164.6766	−0.0002	0.001
8	4	5	$\leftarrow$	7	4	4	6196.7190	0.0011	0.001
8	4	4	$\leftarrow$	7	4	3	6222.2705	−0.0014	0.001
9	0	9	$\leftarrow$	8	0	8	6360.3647	−0.0001	0.001

J'	K'_a	K'_c	$\leftarrow$	J''	K''_a	K''_c	$\nu_{\text{obs.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	exp. error
9	1	9	$\leftarrow$	8	1	8	6354.4312	0.0004	0.001
9	1	8	$\leftarrow$	8	1	7	6788.2245	0.0000	0.001
9	2	8	$\leftarrow$	8	2	7	6697.7347	0.0003	0.001
9	2	7	$\leftarrow$	8	2	6	7169.2727	0.0002	0.001
9	3	7	$\leftarrow$	8	3	6	6918.4394	−0.0001	0.001
9	3	6	$\leftarrow$	8	3	5	7201.8575	−0.0007	0.001
9	4	5	$\leftarrow$	8	4	4	7036.7628	−0.0007	0.001
9	4	6	$\leftarrow$	8	4	5	6979.7631	0.0003	0.001
10	0	10	$\leftarrow$	9	0	9	7043.9065	−0.0004	0.001
10	1	10	$\leftarrow$	9	1	9	7040.9644	0.0004	0.001
10	1	9	$\leftarrow$	9	1	8	7457.6063	−0.0003	0.001
10	2	9	$\leftarrow$	9	2	8	7399.2654	0.0005	0.001
10	2	8	$\leftarrow$	9	2	7	7898.7903	0.0001	0.001
10	3	8	$\leftarrow$	9	3	7	7661.3000	0.0003	0.001
10	3	7	$\leftarrow$	9	3	6	8035.1826	0.0000	0.001
10	4	6	$\leftarrow$	9	4	5	7870.4405	−0.0007	0.001
10	4	7	$\leftarrow$	9	4	6	7759.9294	−0.0010	0.001
10	5	5	$\leftarrow$	9	5	4	7764.7594	−0.0044	0.002
10	5	6	$\leftarrow$	9	5	5	7753.9358	0.0017	0.001
11	0	11	$\leftarrow$	10	0	10	7728.2482	−0.0017	0.001
11	1	11	$\leftarrow$	10	1	10	7726.8280	0.0007	0.001
11	1	10	$\leftarrow$	10	1	9	8129.3959	0.0000	0.001
11	2	10	$\leftarrow$	10	2	9	8094.7065	0.0010	0.001
11	3	9	$\leftarrow$	10	3	8	8392.5769	0.0008	0.002

J'	K'_a	K'_c	$\leftarrow$	J''	K''_a	K''_c	$\nu_{\text{obs.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	exp. error
						$^bR_{-1,1}$			
5	0	5	$\leftarrow$	4	1	4	3503.8192	0.0000	0.002
6	0	6	$\leftarrow$	5	1	5	4238.9512	0.0005	0.002
7	0	7	$\leftarrow$	6	1	6	4953.6633	0.0000	0.001
8	0	8	$\leftarrow$	7	1	7	5655.1132	0.0006	0.002
8	1	7	$\leftarrow$	7	2	6	5763.9780	0.0021	0.002
9	0	9	$\leftarrow$	8	1	8	6348.8112	−0.0006	0.001
10	0	10	$\leftarrow$	9	1	9	7038.2869	−0.0011	0.002
						$^bR_{1,1}$			
6	1	6	$\leftarrow$	5	0	5	4364.9999	−0.0005	0.002
7	1	7	$\leftarrow$	6	0	6	5021.3186	−0.0011	0.002
7	2	6	$\leftarrow$	6	1	5	5775.1087	−0.0018	0.002
8	1	8	$\leftarrow$	7	0	7	5689.7761	−0.0004	0.001
9	1	9	$\leftarrow$	8	0	8	6365.9845	0.0008	0.002
10	1	10	$\leftarrow$	9	0	9	7046.5837	0.0009	0.002

Table S33: Measured frequencies ($\nu_{\text{obs.}}$) and residuals ($\nu_{\text{obs.}} - \nu_{\text{calc.}}$) in MHz of the trihydrate of verbenone 3w-I with the O_1 atom substituted by a ^{18}O atom.

J'	K'_a	K'_c	$\leftarrow$	J''	K''_a	K''_c	$\nu_{\text{obs.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	exp. error
					$^aR_{0,1}$ transitions				
5	0	5	$\leftarrow$	4	0	4	3578.2168	−0.0006	0.002
6	0	6	$\leftarrow$	5	0	5	4243.4597	−0.0008	0.001
6	1	6	$\leftarrow$	5	1	5	4207.9773	−0.0009	0.002
6	1	5	$\leftarrow$	5	1	4	4633.0717	−0.0006	0.002
6	2	4	$\leftarrow$	5	2	3	4739.3913	−0.0015	0.002
7	0	7	$\leftarrow$	6	0	6	4908.7505	−0.0008	0.001
7	1	7	$\leftarrow$	6	1	6	4888.4402	−0.0006	0.001
7	1	6	$\leftarrow$	6	1	5	5334.6405	0.0013	0.002
7	2	6	$\leftarrow$	6	2	5	5182.1312	0.0014	0.002
7	2	5	$\leftarrow$	6	2	4	5536.2505	0.0007	0.002
8	0	8	$\leftarrow$	7	0	7	5576.3883	0.0005	0.001
8	1	8	$\leftarrow$	7	1	7	5565.5717	0.0003	0.001
8	2	7	$\leftarrow$	7	2	6	5887.8311	0.0003	0.002
9	1	9	$\leftarrow$	8	1	8	6240.6380	0.0007	0.001

Table S34: Measured frequencies ($\nu_{\text{obs.}}$) and residuals ($\nu_{\text{obs.}} - \nu_{\text{calc.}}$) in MHz of the trihydrate of verbenone 3w-I with the O_2 atom substituted by a ^{18}O atom.

J'	K'_a	K'_c	$\leftarrow$	J''	K''_a	K''_c	$\nu_{\text{obs.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	exp. error
					$^aR_{0,1}$ transitions				
6	0	6	$\leftarrow$	5	0	5	4236.6473	0.0002	0.002
6	1	5	$\leftarrow$	5	1	4	4608.6941	0.0000	0.001
6	2	5	$\leftarrow$	5	2	4	4442.0430	0.0004	0.002
6	3	4	$\leftarrow$	5	3	3	4525.2313	0.0018	0.002
7	0	7	$\leftarrow$	6	0	6	4900.7179	0.0001	0.001
7	1	7	$\leftarrow$	6	1	6	4876.5891	0.0009	0.002
7	2	6	$\leftarrow$	6	2	5	5157.4228	0.0003	0.002
7	2	5	$\leftarrow$	6	2	4	5486.3212	−0.0012	0.002
8	0	8	$\leftarrow$	7	0	7	5566.6834	0.0001	0.001
8	1	8	$\leftarrow$	7	1	7	5553.2079	−0.0003	0.002
8	2	7	$\leftarrow$	7	2	6	5863.3256	−0.0011	0.002
9	0	9	$\leftarrow$	8	0	8	6234.7525	−0.0002	0.001
9	1	9	$\leftarrow$	8	1	8	6227.5975	−0.0006	0.002

Table S35: Measured frequencies ($\nu_{\text{obs.}}$) and residuals ($\nu_{\text{obs.}} - \nu_{\text{calc.}}$) in MHz of the trihydrate of verbenone 3w-I with the O_3 atom substituted by a ^{18}O atom.

J'	K'_a	K'_c	$\leftarrow$	J''	K''_a	K''_c	$\nu_{\text{obs.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	exp. error
					$^aR_{0,1}$ transitions				
5	0	5	$\leftarrow$	4	0	4	3583.9785	−0.0024	0.002
6	0	6	$\leftarrow$	5	0	5	4250.8214	−0.0009	0.002
6	2	4	$\leftarrow$	5	2	3	4741.3769	−0.0029	0.002
7	0	7	$\leftarrow$	6	0	6	4917.6706	−0.0008	0.002
7	1	7	$\leftarrow$	6	1	6	4897.4016	−0.0001	0.001
7	1	6	$\leftarrow$	6	1	5	5339.7814	0.0000	0.002
7	2	6	$\leftarrow$	6	2	5	5188.2904	0.0004	0.002
7	2	5	$\leftarrow$	6	2	4	5538.7047	0.0011	0.002
8	0	8	$\leftarrow$	7	0	7	5586.8342	−0.0004	0.001
8	1	8	$\leftarrow$	7	1	7	5576.0229	0.0005	0.001
8	2	6	$\leftarrow$	7	2	5	6313.9068	0.0012	0.002
9	0	9	$\leftarrow$	8	0	8	6258.0830	0.0001	0.002
9	1	9	$\leftarrow$	8	1	8	6252.5905	0.0014	0.002
9	2	8	$\leftarrow$	8	2	7	6592.8806	0.0035	0.005

Table S36: Measured frequencies ($\nu_{\text{obs.}}$) and residuals ($\nu_{\text{obs.}} - \nu_{\text{calc.}}$) in MHz of the trihydrate of verbenone 3w-I with the O_1 and O_2 atoms substituted by ^{18}O atoms.

J'	K'_a	K'_c	←	J''	K''_a	K''_c	$\nu_{\text{obs.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	exp. error
					$^aR_{0,1}$ transitions				
5	0	5	←	4	0	4	3510.6965	0.0007	0.002
5	1	5	←	4	1	4	3452.5953	0.0019	0.002
5	1	4	←	4	1	3	3818.5164	0.0012	0.002
5	2	3	←	4	2	2	3833.0064	0.0029	0.002
6	0	6	←	5	0	5	4163.7318	0.0007	0.002
6	1	6	←	5	1	5	4125.2587	0.0008	0.002
6	1	5	←	5	1	4	4538.1608	0.0000	0.002
6	2	5	←	5	2	4	4372.5169	0.0021	0.002
6	2	4	←	5	2	3	4627.3524	−0.0018	0.002
7	0	7	←	6	0	6	4815.9617	0.0003	0.001
7	1	7	←	6	1	6	4793.1420	0.0008	0.002
7	1	6	←	6	1	5	5230.9278	0.0002	0.002
7	2	6	←	6	2	5	5075.5732	0.0005	0.002
7	2	5	←	6	2	4	5409.2410	−0.0018	0.002
8	0	8	←	7	0	7	5470.2187	0.0003	0.001
8	1	8	←	7	1	7	5457.6467	0.0000	0.002
8	1	7	←	7	1	6	5898.0981	−0.0005	0.002
8	2	7	←	7	2	6	5768.9711	−0.0005	0.001
9	0	9	←	8	0	8	6126.5708	−0.0018	0.002
10	1	10	←	9	1	9	6781.0333	−0.0026	0.002

Table S37: Measured frequencies ($\nu_{\text{obs.}}$) and residuals ($\nu_{\text{obs.}} - \nu_{\text{calc.}}$) in MHz of the trihydrate of verbenone 3w-I with the O_1 and O_3 atoms substituted by ^{18}O atoms.

J'	K'_a	K'_c	$\leftarrow$	J''	K''_a	K''_c	$\nu_{\text{obs.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	exp. error
					$^aR_{0,1}$ transitions				
5	1	5	$\leftarrow$	4	1	4	3468.4493	0.0000	0.002
5	1	4	$\leftarrow$	4	1	3	3846.3826	−0.0006	0.002
5	2	4	$\leftarrow$	4	2	3	3685.3683	−0.0036	0.005
6	0	6	$\leftarrow$	5	0	5	4176.3938	−0.0007	0.002
6	1	6	$\leftarrow$	5	1	5	4142.7613	0.0000	0.001
6	2	5	$\leftarrow$	5	2	4	4400.4235	−0.0002	0.002
7	0	7	$\leftarrow$	6	0	6	4831.2327	−0.0002	0.002
7	1	7	$\leftarrow$	6	1	6	4812.2600	−0.0002	0.001
7	1	6	$\leftarrow$	6	1	5	5253.2337	−0.0008	0.002
7	2	6	$\leftarrow$	6	2	5	5104.9848	0.0000	0.001
7	2	5	$\leftarrow$	6	2	4	5460.7198	−0.0001	0.002
8	0	8	$\leftarrow$	7	0	7	5488.4789	−0.0001	0.001
8	1	8	$\leftarrow$	7	1	7	5478.5149	0.0002	0.001
8	1	7	$\leftarrow$	7	1	6	5916.1412	0.0005	0.002
8	2	7	$\leftarrow$	7	2	6	5799.1026	0.0007	0.002
8	2	6	$\leftarrow$	7	2	5	6222.0344	0.0005	0.002
9	0	9	$\leftarrow$	8	0	8	6147.7762	0.0000	0.002
9	2	8	$\leftarrow$	8	2	7	6483.7525	0.0009	0.002
10	0	10	$\leftarrow$	9	0	9	6808.3603	−0.0002	0.002
10	1	10	$\leftarrow$	9	1	9	6805.9476	0.0004	0.002

Table S38: Measured frequencies ($\nu_{\text{obs.}}$) and residuals ($\nu_{\text{obs.}} - \nu_{\text{calc.}}$) in MHz of the trihydrate of verbenone 3w-I with the O_2 and O_3 atoms substituted by ^{18}O atoms.

J'	K'_a	K'_c	$\leftarrow$	J''	K''_a	K''_c	$\nu_{\text{obs.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	exp. error
					$^aR_{0,1}$ transitions				
6	0	6	$\leftarrow$	5	0	5	4170.8338	0.0007	0.001
6	1	6	$\leftarrow$	5	1	5	4132.4389	0.0007	0.002
6	1	5	$\leftarrow$	5	1	4	4541.3161	−0.0010	0.002
6	2	5	$\leftarrow$	5	2	4	4377.0531	0.0014	0.002
6	2	4	$\leftarrow$	5	2	3	4628.6562	0.0000	0.002
7	0	7	$\leftarrow$	6	0	6	4824.5846	−0.0002	0.002
7	1	7	$\leftarrow$	6	1	6	4801.7535	0.0004	0.001
7	1	6	$\leftarrow$	6	1	5	5235.5801	0.0010	0.002
7	2	6	$\leftarrow$	6	2	5	5081.2395	0.0008	0.002
7	2	5	$\leftarrow$	6	2	4	5410.9231	0.0000	0.002
8	0	8	$\leftarrow$	7	0	7	5480.3218	−0.0002	0.002
8	1	8	$\leftarrow$	7	1	7	5467.7140	0.0004	0.002
8	1	7	$\leftarrow$	7	1	6	5904.4939	−0.0005	0.002
8	2	7	$\leftarrow$	7	2	6	5775.8899	0.0000	0.002
8	2	6	$\leftarrow$	7	2	5	6173.9521	−0.0004	0.002
9	0	9	$\leftarrow$	8	0	8	6138.1365	−0.0020	0.002
9	1	9	$\leftarrow$	8	1	8	6131.5139	−0.0014	0.002
9	2	8	$\leftarrow$	8	2	7	6461.5890	−0.0011	0.002

Table S39: Measured frequencies ($\nu_{\text{obs.}}$) and residuals ($\nu_{\text{obs.}} - \nu_{\text{calc.}}$) in MHz of the trihydrate of verbenone 3w-I with all oxygen atoms of water substituted by ^{18}O atoms.

J'	K'_a	K'_c	$\leftarrow$	J''	K''_a	K''_c	$\nu_{\text{obs.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	exp. error
					$^aR_{0,1}$ transitions				
5	0	5	$\leftarrow$	4	0	4	3457.4936	0.0010	0.002
5	1	5	$\leftarrow$	4	1	4	3401.4687	0.0004	0.002
5	1	4	$\leftarrow$	4	1	3	3766.1262	−0.0006	0.001
5	2	4	$\leftarrow$	4	2	3	3608.8873	0.0022	0.005
5	2	3	$\leftarrow$	4	2	2	3784.5738	−0.0029	0.002
6	0	6	$\leftarrow$	5	0	5	4100.2490	−0.0005	0.001
6	1	6	$\leftarrow$	5	1	5	4063.7031	0.0001	0.001
6	1	5	$\leftarrow$	5	1	4	4473.9399	−0.0002	0.002
6	2	5	$\leftarrow$	5	2	4	4310.7364	0.0005	0.002
6	2	4	$\leftarrow$	5	2	3	4568.2703	−0.0010	0.002
6	3	3	$\leftarrow$	5	3	2	4450.0472	0.0014	0.002
7	0	7	$\leftarrow$	6	0	6	4742.5667	−0.0001	0.001
7	1	7	$\leftarrow$	6	1	6	4721.2042	0.0002	0.001
7	1	6	$\leftarrow$	6	1	5	5154.3864	0.0002	0.002
7	2	6	$\leftarrow$	6	2	5	5002.9477	0.0005	0.001
7	2	5	$\leftarrow$	6	2	4	5338.6831	−0.0010	0.002
7	3	5	$\leftarrow$	6	3	4	5129.0524	0.0012	0.002
7	3	4	$\leftarrow$	6	3	3	5235.2150	−0.0013	0.002
8	0	8	$\leftarrow$	7	0	7	5387.0114	−0.0002	0.001
8	1	8	$\leftarrow$	7	1	7	5375.4058	0.0002	0.001
8	1	7	$\leftarrow$	7	1	6	5809.4458	0.0002	0.002
8	2	7	$\leftarrow$	7	2	6	5685.3952	0.0003	0.002
8	2	6	$\leftarrow$	7	2	5	6088.7523	−0.0007	0.002
8	3	6	$\leftarrow$	7	3	5	5853.8559	0.0013	0.002
8	3	5	$\leftarrow$	7	3	4	6035.3858	0.0001	0.001
9	0	9	$\leftarrow$	8	0	8	6033.5212	−0.0003	0.001
9	1	9	$\leftarrow$	8	1	8	6027.5198	0.0000	0.001
9	1	8	$\leftarrow$	8	1	7	6448.5572	0.0000	0.002

J'	K'_a	K'_c	←	J''	K''_a	K''_c	$\nu_{\text{obs.}}$	$\nu_{\text{obs.}} - \nu_{\text{calc.}}$	exp. error
9	2	8	←	8	2	7	6358.7775	−0.0002	0.002
9	2	7	←	8	2	6	6813.0330	−0.0008	0.002
9	3	7	←	8	3	6	6569.8981	0.0009	0.002
9	3	6	←	8	3	5	6839.0059	−0.0004	0.002
10	0	10	←	9	0	9	6681.4103	−0.0018	0.002
10	1	9	←	9	1	8	7082.8970	0.0008	0.002
10	2	9	←	9	2	8	7024.4795	0.0015	0.002
10	3	8	←	9	3	7	7275.5984	0.0005	0.002
11	0	11	←	10	0	10	7330.0979	−0.0024	0.002
11	1	11	←	10	1	10	7328.6405	−0.0008	0.002
11	1	10	←	10	1	9	7719.2776	0.0004	0.002
11	2	10	←	10	2	9	7684.2409	0.0014	0.002
							$^{b}R_{-1,1}$		
8	1	7	←	7	2	6	5460.3284	0.0012	0.002
9	0	9	←	8	1	8	6021.7622	0.0002	0.002
							$^{b}R_{1,1}$		
7	1	7	←	6	0	6	4765.9327	0.0001	0.002
8	1	8	←	7	0	7	5398.7714	0.0001	0.002
9	1	9	←	8	0	8	6039.2795	0.0001	0.002

Table S40: Decomposition of the interaction energy between verbenone and water as calculated at the SAPT0 / jun-cc-PVDZ level of theory, values in kJ mol^{-1}

	E_{elec}	E_{exch}	E_{ind}	E_{disp}	E_{SAPT0}	E_{BSSE}
1w-I	−47.69	40.16	−13.44	−13.62	−34.58	−25.22
1w-II	−51.02	42.51	−14.30	−11.30	−34.11	−25.61
2w-I	−72.93	62.65	−25.15	−19.15	−54.59	−42.17
2w-II(a)	−72.14	58.51	−23.61	−15.52	−52.77	−40.71