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Supporting Information

A General Treatment to Study Molecular Complexes Stabilized by Hydrogen-, Halogen-, and Carbon-Bond Networks: Experiment and Theory of $(CH_2F_2)_n\cdots(H_2O)_m$

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1] **PROTOCOL** FOR COMPUTATIONAL SCREENING

The starting arrangements for trimers and tetramers (shown after) were prepared with an "in house" code specifically implemented for this kind of systems. All QM calculations were carried out with the Gaussian09 suite.[1] The DFT optimizations were performed with the Dunning's correlation consistent aug-cc-pvTz basis set, whereas MP2 calculations were carried out with the 6-311++G(d,p) basis set. In both DFT and MP2 energy minimizations, all internal degrees of freedom were optimized without imposing any symmetry constraint.

The computational protocol adopted to explore the configurational space of the investigated trimers and tetramers is sketched for **D2W2** clusters in Figure S1 and briefly outlined in the following.

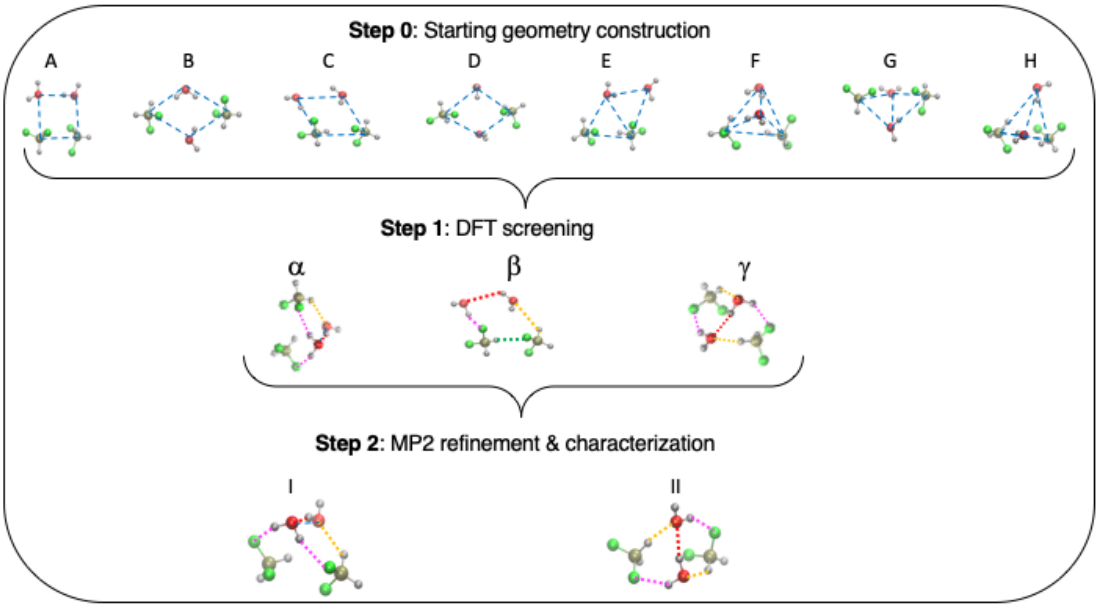


Figure S1: Computational screening protocol set up for the **D2W2** tetramer.

Step 0: Starting geometry construction

A number of plausible configurations was prepared by disposing the monomer centers of mass based on symmetry considerations (planar, tetragonal, triangular, *etc.*) and orienting the D-H bonds according to the possible favorable WHB networks allowed by the different dispositions. All the attempted starting conformation are separately displayed for **DW2**, **D2W, DW3** and **D2W2** clusters in Figures S2, S4, S6 and S8, respectively.

Step 1: DFT screening

The computational convenience of the DFT technique is exploited to perform, for each chosen cluster arrangement prepared in Step 0, a preliminary optimization, carried out at B97D/aug-cc-pvTz level. The resulting conformers were classified according to their structure, rotational constants and binding energies.

Step 2: MP2 refinement

The structure of the most stable conformers was further refined at MP2/6-311++G(d,p) level. Eventually, the MP2 most stable optimized structures are collected, and characterized through their binding energies and structural parameters.

The same procedure was applied to all species, namely **DW2**, **D2W, DW3** and **D2W2.**

2] DETAILS ON **DW2** CLUSTERS

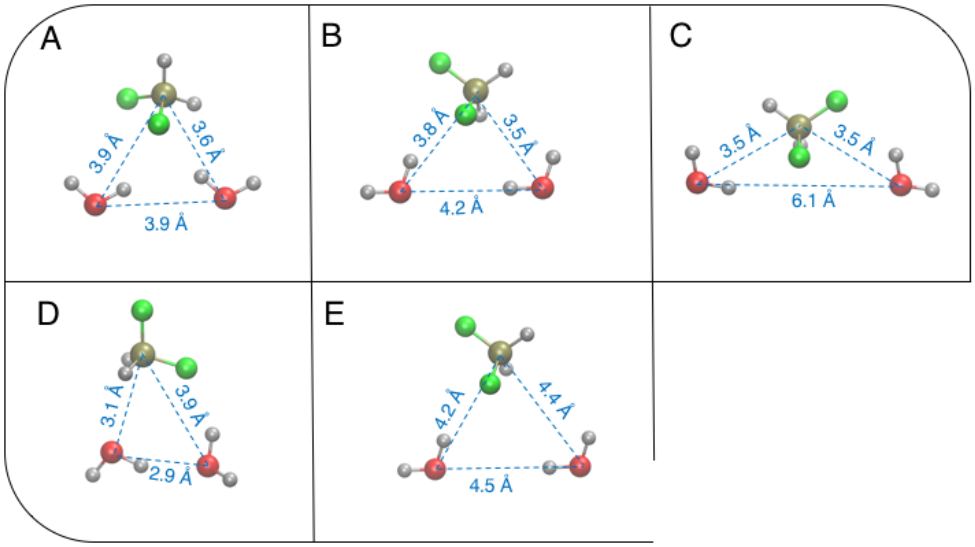


Figure S2: Starting structures for the $CH_2F_2\cdots[H_2O]_2$ (**DW2**) trimer. The and O···O and C···O distances that characterize the cluster structure are displayed with blue dashed lines.

Five starting configurations (A-E, displayed in Figure S2) were initially considered for the of **DW2** clusters, and subjected to the computational screening protocol described in Section 1]. All starting arrangements eventually collapsed into two different classes, namely triangular or linear dispositions. Among these, the three most stable conformers found at MP2 level are shown in Figure S3, where trimers I and III belong to the former class, while II, less stable, displays a quasi linear geometry. Both MP2 computed binding energies and rotational constants are reported in Table S1 for all three conformers. It should be noted that cluster I and III have practically the same energy and are characterized by a very similar structure and WHB network. Yet, they exhibit significantly different rotational constants and dipole moments, confirming the challenges that this kind of computational screening might encounter.

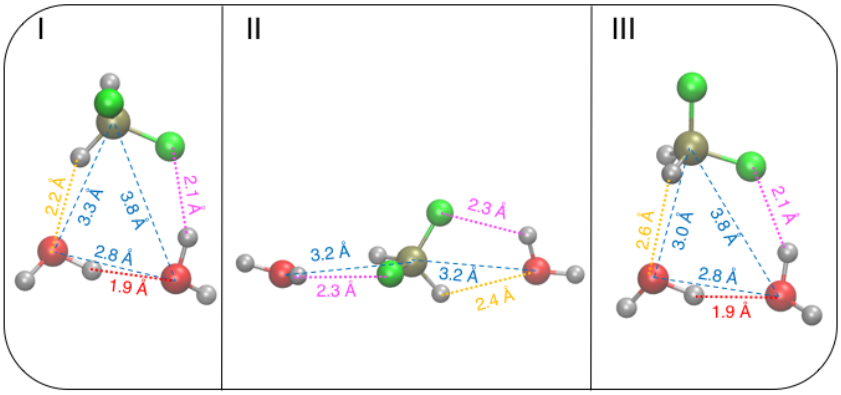


Figure S3: Most stable structures for **DW2** trimers. The O···O and C··O· distances that characterize the cluster structure are displayed with blue dashed lines, whereas the different WHB, whose distance is less than 3.0 Å, are evidenced with dotted lines in different colors (OH···O red; O-H···F magenta; C-H···O orange).

Table S1: Relative energies ΔE (with respect to the most stable conformer), binding energies (BE), rotational constants (A, B and C) and electric dipole components (μa, μb, μc), computed for the most stable structures of **DW2** trimers shown in Figure S3. The best matching conformer is evidence in bold.

Cluster	**ΔE** kJ/mol	**BE** kJ/mol	**A** MHz	**B** MHz	**C** MHz	**μ_a** D	**μ_b** D	**μ_c** D
I	0.0	-41.7	4441	1872	1456	-1.2	0.6	1.2
II	17.1	-25.1	8383	1238	1229	0.0	0.0	0.9
III	**0.0**	**-41.7**	**5560**	**1736**	**1339**	**2.1**	**0.0**	**0.3**

3] DETAILS ON **D2W CLUSTERS**

For the computational screening of **DW2** clusters, six starting configurations, displayed in Figure S4, were selected and optimized through the proposed screening protocol. As for the **DW2** trimer, all arrangements collapsed into two either triangular or linear dispositions. As done previously, the three most stable conformers found at MP2 level are shown in Figure S5, but at difference with **DW2**, no **D2W** linear stable cluster was found, resulting instead into three different triangular conformers. MP2 computed binding energies and rotational constants of the three clusters are reported in Table S2.

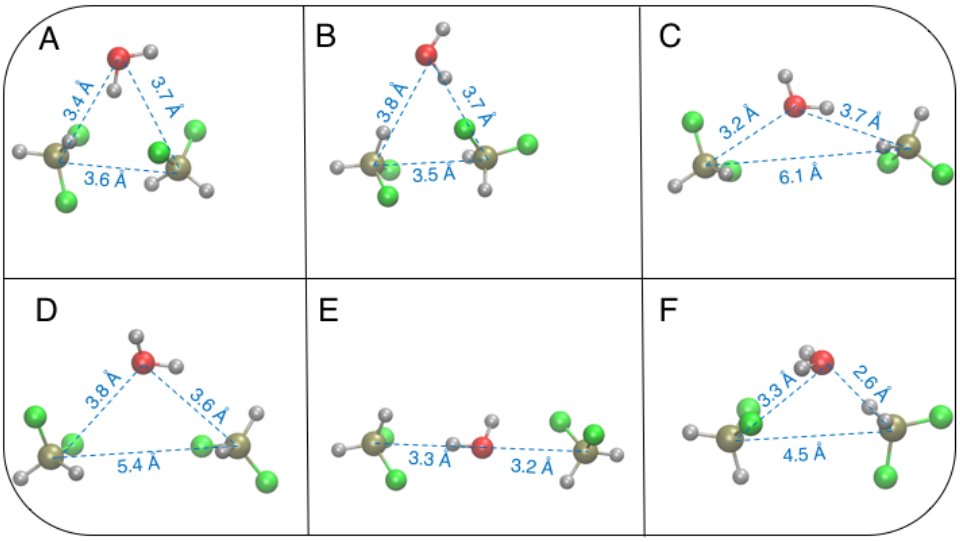


Figure S4: Starting structures for the $[CH_2F_2]_2 \cdots H_2O$ (**D2W**) trimer. The C···C and C···O distances that characterize the cluster structure are displayed with blue dashed lines.

Table S2: Relative energies ΔE (with respect to the most stable conformer), binding energies (BE), rotational constants (A, B and C) and electric dipole components (μ_a, μ_b, μ_c), computed for the most stable structures of D2W trimers shown in Figure S5. The best matching conformer is evidence in bold.

Cluster	**ΔE** kJ/mol	**BE** kJ/mol	**A** MHz	**B** MHz	**C** MHz	**μ_A** D	**μ_B** D	**μ_C** D
I	2.5	-24.7	2585	1056	1037	-0.5	-0.7	0.0
II	**0.0**	**-28.0**	**2304**	**1103**	**874**	**1.6**	**0.4**	**-0.1**
III	4.6	-23.4	4282	478	452	-0.6	0.4	2.2

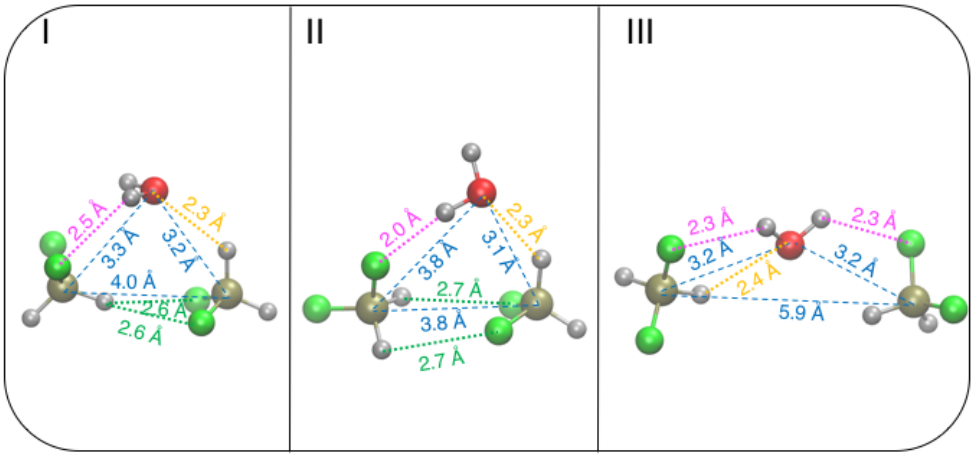


Figure S5: Most stable structures for **D2W** trimers. The C···O and C···C distances that characterize the cluster structure are displayed with blue dashed lines, whereas the different WHB, whose distance is less than 3.0 Å, are evidenced with dotted lines in different colors (O-H···F magenta; C-H···O orange; C-H···F green).

4] DETAILS ON **DW3 CLUSTERS**

Nine different starting clusters, labeled A to I, were prepared as shown in Figure S6. The resulting optimized conformers were classified according to their structure and energies, revealing either planar or tetrahedral-like arrangements. Among these, the three most stable conformers found at MP2 level are shown in Figure S7, and can be classified as tetrahedral (I and II) or planar (III), being the former more stable than the latter. MP2 computed binding energies and rotational constants of the three clusters are reported in Table S3.

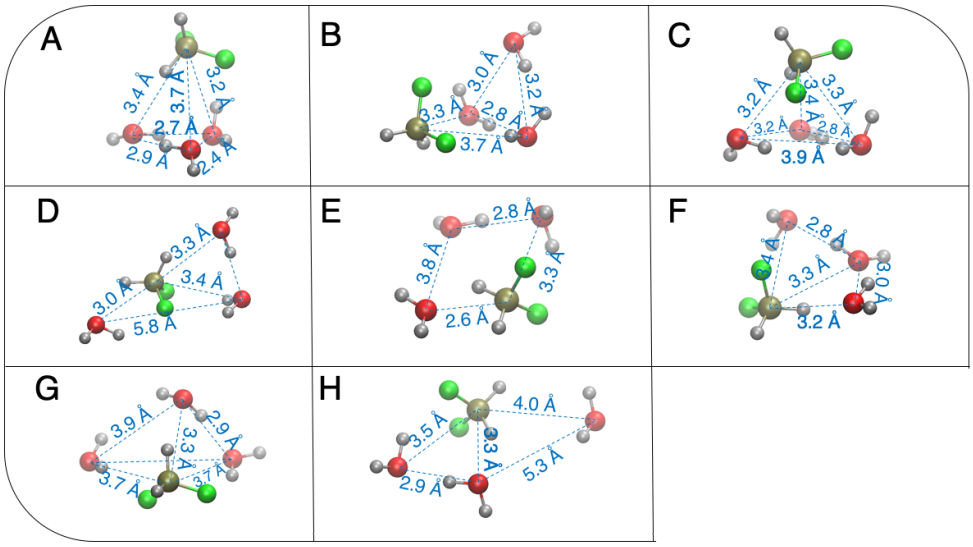


Figure S6: Starting structures for the $CH_2F_2 \cdots [H_2O]_3$ (**DW3**) tetramers. The O···O and C···O distances that characterize the cluster structure are displayed with blue dashed lines.

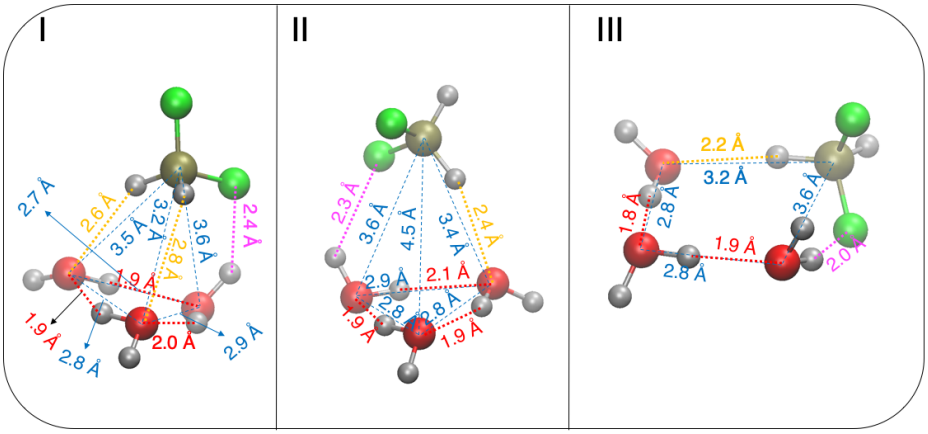


Figure S7: Most stable structures for **DW3** tetramers. The O···O and C···O distances that characterize the cluster structure are displayed with blue dashed lines, whereas the different WHB, whose distance is less than 3.0 Å, are evidenced with dotted lines in different colors (OH···O red; O-H···F magenta; C-H···O orange).

Table S3: Relative energies ΔE (with respect to the most stable conformer), binding energies (BE), rotational constants (A, B and C) and electric dipole components (μ_a, μ_b, μ_c), computed for the most stable structures of DW3 tetramers shown in Figure S7. The best matching conformer is evidence on bold.

Cluster	**ΔE**	**BE**	**A**	**B**	**C**	**μ_A**	**μ_B**	**μ_C**
	kJ/mol	kJ/mol	MHz	MHz	MHz	D	D	D
I	**0.0**	**-73.5**	**2801**	**1213**	**1140**	**1.2**	**1.3**	**-1.4**
II	2.3	-71.5	2768	1158	1123	2.0	-1.1	0.2
III	0.2	-72.6	2336	1370	1018	-1.9	-0.2	1.2

5] DETAILS ON **D2W2 CLUSTERS**

Eight different starting clusters (A-H, displayed in Figure S8) were prepared according to different dispositions, namely tetrahedral, "bended", planar and elongated. After MP2 optimization, two tetrahedral complexes were identified as the most stable. Their structures are displayed in Figure S9, while their binding energies and structural parameters are reported in Table S4.

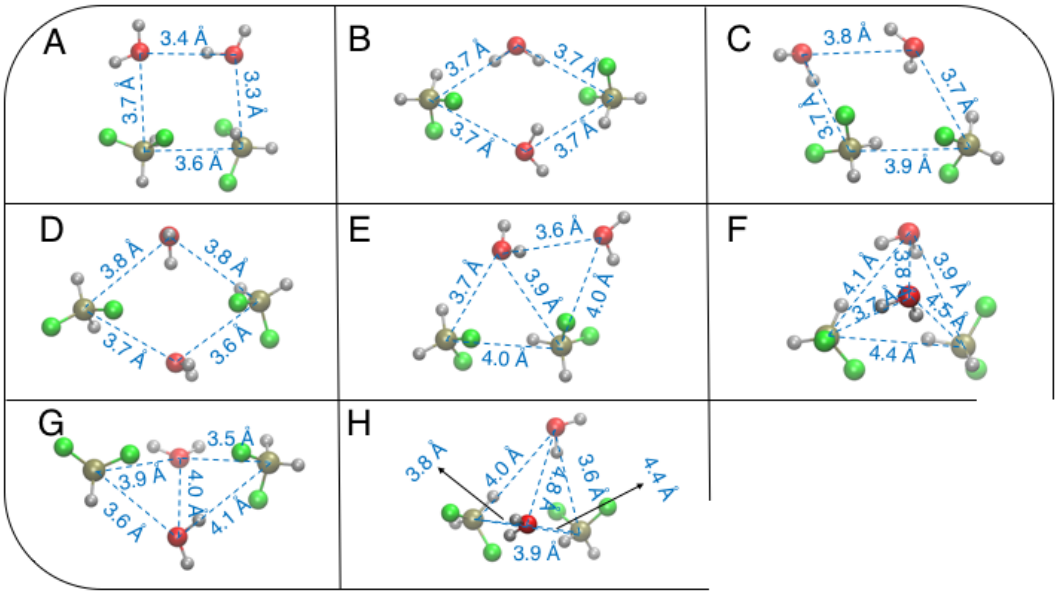


Figure S8: Starting structures for the $[CH_2F_2]_2 \cdots [H_2O]_2$ (**D2W2**) tetramer. The and O···O, C···C and C···O distances that characterize the cluster structure are displayed with blue dashed lines.

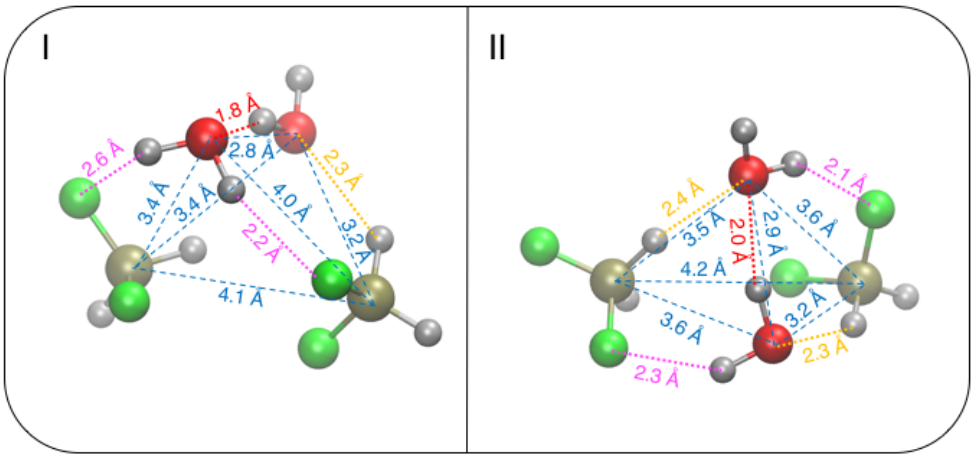


Figure S9: Most stable structures for D2W2 tetramers. The O···O, C···O and C···C distances that characterize the cluster structure are displayed with blue dashed lines, whereas the different WHB, whose distance is less than 3.0 Å, are evidenced with dotted lines in different colors (OH···O red; O-H···F magenta; C-H···O orange; C-H···F green).

Table S4: Relative energies ΔE (with respect to the most stable conformer), binding energies (BE), rotational constants (A, B and C) and electric dipole components (μ_a, μ_b, μ_c), computed for the most stable structures of D2W2 tetramers shown in Figure S9. The best matching conformer is evidence on bold.

Cluster	**ΔE** kJ/mol	**BE** kJ/mol	**A** MHz	**B** MHz	**C** MHz	**μ_A** D	**μ_B** D	**μ_C** D
I	0.0	-54.0	1665	950	834	0.8	1.0	-1.4
II	**2.9**	**-53.0**	**1744**	**737**	**700**	**2.7**	**-0.6**	**1.2**

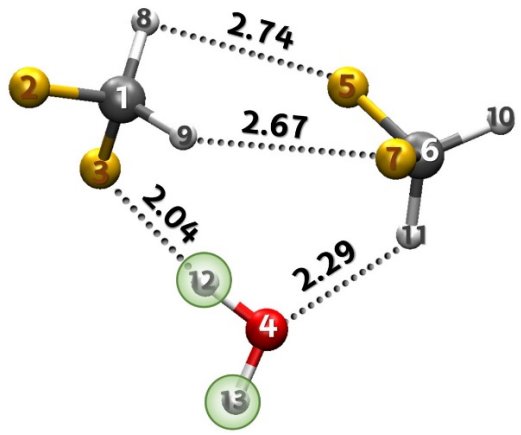
6] EXPERIMENTAL SECTION

The microwave spectra of parent species were performed in Pate's group at the University of Virginia using a CP-FTMW spectrometer, which covers the frequency ranges 2–8 GHz, while the deuterated species were measured by means of the CP-FTMW in Cocinero's group at the University of the Basque Country (UPV/EHU), which covers the frequency range 6-18 GHz. Both equipment were already described in details elsewhere.[2,3]

The DFM sample was obtained from Sigma Aldrich. In the first experiment, a gas mixture of 1% CH_2F_2 in Ne was used at a backing pressure of 350 kPa, passed through a container with water and then adiabatically expanded into the spectrometer by a few hundreds μs duration pulses. In the second one, the D_2O was purchased from Sigma Aldrich and the deuterated species was achieved by mixing D_2O and H_2O with 1:1 ratio. A gas mixture of 1% DFM in He with a stagnant pressure of 300 kPa was expanded into the cavity after passing over the water reservoir.

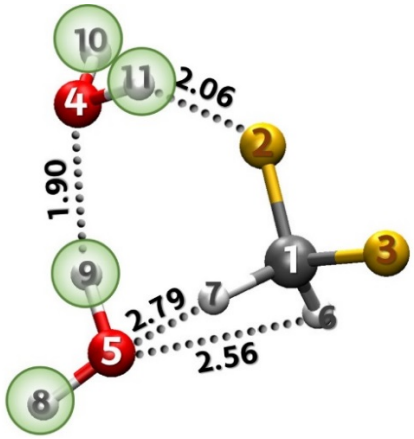
7] **STRUCTURAL RESULTS** OF THE OBSERVED CLUSTERS

Table S5: Comparison between experimental (r_s) and calculated (r_e, MP2/6-311++G(d,p)) principal axes coordinates of the corresponding hydrogen atoms. The values of the r_s coordinates are calculated from the hypothetically unsplit frequency, obtained considering the average of the rotational constants of the v=0 and v=1 states for the parent species. The error in parenthesis are expressed in units of the last decimal digits.



D2W	H12		H13	
	r_s	r_e	r_s	r_e
a/Å	±0.924*i(2)	0.046	±0.186*i(9)	0.680
b/Å	±1.6915(9)	2.073	±2.9223(6)	3.096
c/Å	±0.916(2)	-0.079	±1.204(1)	-0.996

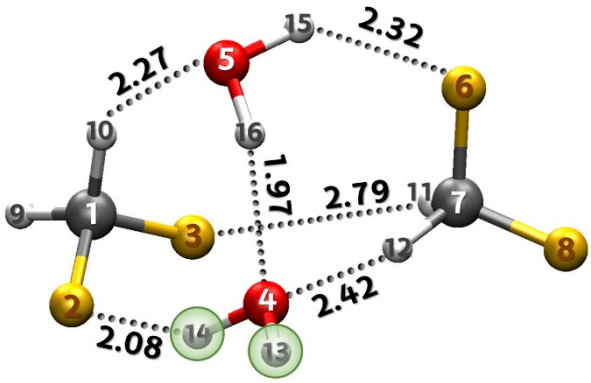
Table S6: Comparison between experimental (r_s) and calculated (r_e, MP2/6-311++G(d,p)) principal axes coordinates of the corresponding hydrogen atoms. The values of the r_s coordinates are calculated from the hypothetically unsplit frequency, obtained considering the average of the rotational constants of the v=0 and v=1 states for the parent species. The error in parenthesis are expressed in units of the last decimal digits.



DW2	H8		H9		H10*		H11	
	r_s	r_e	r_s	r_e	r_s	r_e	r_s	r_e
a/Å	±2.1653(8)	2.091	±2.0425(9)	2.042	±2.8411(6)	2.882	±1.159(1)	1.530
b/Å	±2.3088(7)	2.314	±0.776(2)	0.842	±1.566(1)	-1.569	±1.427(1)	-1.340
c/Å	±0.217(8)	0.346	±0.16(1)	-0.038	±0.371(5)	-0.629	±0.180(9)	0.027

* For this atom, the principal axes coordinates have been calculated using as parent species the bi-deuterated D1011 one, and considering the monosubstituion with the D11 isotopologue. For the latter, the average of the rotational constants of the v=0 and v=1 states was used.

Table S7: Comparison between experimental (r_s) and calculated (r_e, MP2/6-311++G(d,p)) principal axes coordinates of the corresponding hydrogen atoms. The error in parenthesis are expressed in units of the last decimal digits.



D2W2	H13		H14	
	r_s	r_e	r_s	r_e
a/Å	±0.549(5)	0.522	±1.396(2)	1.355
b/Å	±2.057(1)	2.199	±1.210(3)	1.099
c/Å	±1.645(2)	-2.196	±1.309(3)	-1.550

8] **BINDING ENERGY** CONSIDERATIONS

Table S8: Comparison of the Binding Energies (BE, kJ/mol) values calculated at the MP2/6-311++G(d,p) level and obtained summing all the BCPs contributions for each cluster.

	MP2/6-311++G(d,p) Counterpoise corrected	QTAIM – Sum of the BCPs	EXPERIMENTAL*
	kJ/mol	kJ/mol	kJ/mol
W dimer	-	-	13.2
DFM dimer	-8.4	-24.5	6.6
DW	-12.9	-18.1	7.5
D2W	-28.0	-39.7	-
DW2	-41.7	-53.2	-
D2W2	-53.0	-75.7	-
DW3	-73.5	-102.4	

* The values reported corresponds to the dissociation energy measured for the water dimer,[4] the DFM dimer,[5] and the DW adduct.[6] The last two values derived from the estimation of the stretching force constant and assuming a Lennard-Jones potential function approximation.

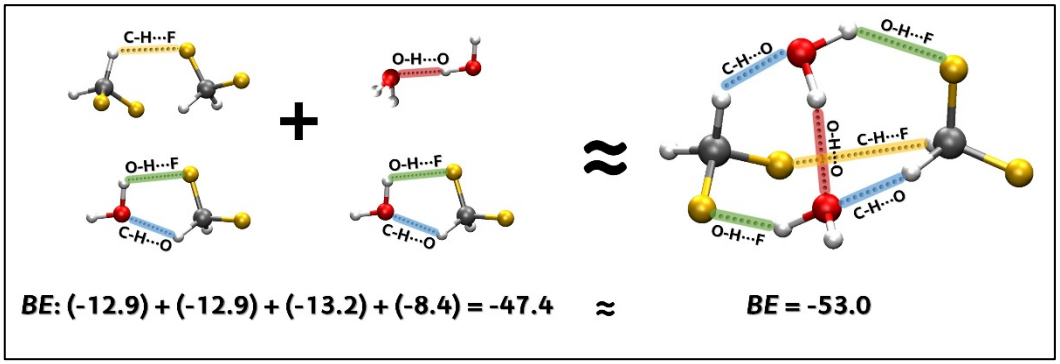


Figure S10: Considerations on the **D2W2** binding interactions. Looking at the values reported in Table S8, the BE calculated for the **D2W2** cluster is quite similar to the sum of the different dimers (DFM dimer, W dimer, and DW dimer) which are involved in determine the tetramer interactions. It can be also pointed out that the BE of the dimers involving the water moiety (W dimer and DW dimer) present a very similar BE rather than the DFM dimer that is characterized by weaker non-covalent interactions. As expected, since the number of interactions increases, the WHB network that keeps together the tetramer is more stabilizing rather than the interactions characterizing the separated dimers.

9] **SPECTROSCOPIC PARAMETERS** OF THE ASSIGNED CLUSTERS AND THEIR ISOTOPOLOGUES

Table S9: Experimental rotational parameters of the parent and deuterated species of **D2W**. The labelling of the atoms follows the ones displayed in Table S5. The error in parenthesis are in unit of the last digit. σ is the root-mean-square deviation of the fit. N is the number of the fitted transitions.

D2W	Parent		D_2O	D12	D13
	v=0	v=1			
A/MHz	2248.046(7)	2248.189(7)	2124.00(4)	2211.654(3)	2152.63(3)
B/MHz	1096.505(1)	1096.513(1)	1093.180(2)	1096.613(1)	1093.381(1)
C/MHz	860.5630(6)	860.5101(6)	847.471(2)	857.5871(7)	848.144(1)
D_J/kHz	2.512(8)	2.501(8)	7.30(3)	3.563(4)	4.13(1)
D_{JK}/kHz	36.73(5)	36.35(6)	85.2(2)	51.26(3)	59.5(1)
D_K/kHz	-21(3)	-21(3)	-159(6)	-41.1(3)	-66(6)
d_1/kHz	-0.082(3)	-0.084(3)	-0.150(8)	-0.060(4)	-0.076(8)
d_2/kHz	0.809(5)	0.797(5)	3.77(1)	1.395(2)	1.67(1)
H_J/Hz			-0.7(2)		
σ/kHz	10.113		14.534	12.147	10.419
N	121		35	57	31

Table S10: Experimental rotational parameters of the parent and deuterated species of **DW2**. The labelling of the atoms follows the ones displayed in Table S6. The error in parenthesis are in unit of the last digit. σ is the root-mean-square deviation of the fit. N is the number of the fitted transitions.

DW2	Parent		$(D_2O)_2$		D8	
	v=0	v=1	v=0	v=1	v=0	v=1
A/MHz	5249.79(8)	5249.99(9)	4707.62(7)	4707.44(8)	4981.8(1)	4977.5(6)
B/MHz	1729.538(3)	1729.659(3)	1628.872(4)	1628.863(4)	1701.261(8)	1701.62(2)
C/MHz	1316.198(2)	1316.167(3)	1225.459(3)	1225.437(3)	1282.953(4)	1282.78(1)
D_J/kHz	1.30(2)	1.22(2)	1.03(3)	0.94(3)	1.01(6)	0.6(1)
D_{JK}/kHz	12.3(1)	13.7(2)	10.6(1)	10.9(2)	13.5(9)	26(1)
d_1/kHz	-0.40(2)	-0.52(2)	-0.23(3)	-0.34(3)	-0.30(6)	-4.2(3)
d_2/kHz	-0.11(1)	-0.11(1)		-0.13(2)	-0.12(4)	
σ/kHz	9.934		11.882		11.5	
N	43		35		21	

DW2	D9		D11		D8,9	
	v=0	v=1	v=0	v=1	v=0	v=1
A/MHz	5217.8(1)	5215.5(2)	5141.6(1)	5139.8(1)	4959.9(1)	4961.3(4)
B/MHz	1705.096(2)	1705.220(3)	1721.435(5)	1721.472(8)	1677.400(6)	1677.550(9)
C/MHz	1300.103(2)	1300.090(4)	1304.753(4)	1304.750(5)	1268.016(5)	1267.967(7)
D_J/kHz	1.10(2)	0.45(3)	1.27(5)	1.14(6)	0.99(4)	1.2(1)
D_{JK}/kHz	13.2(5)	19.2(7)	8(1)	12(1)	13.1(6)	17(1)
d_1/kHz	-0.34(2)	-0.97(3)	-0.39(4)	-0.51(5)	-0.28(5)	-0.7(1)
d_2/kHz	-0.09(3)	-0.41(5)			-0.10(3)	-1.1(1)
σ/kHz	8.837		13.82		9.828	
N	31		25		23	

DW2	D8,11	D9,11	D10,11
A/MHz	4876.4(1)	5108.22(8)	5001.0(3)
B/MHz	1694.197(4)	1697.578(3)	1674.38(1)
C/MHz	1272.014(3)	1288.997(2)	1269.668(8)
D_J/kHz	1.05(3)	1.16(2)	7.14(9)
D_{JK}/kHz	12.3(5)	11.6(4)	15(1)
d_1/kHz	-0.34(3)	-0.33(2)	-5.0(1)
d_2/kHz	-0.12(3)		-0.12(7)
σ/kHz	10.543	9.876	15.841
N	15	15	11

DW2	D8,9,11	D9,10,11
A/MHz	4853.63(8)	4960(1)
B/MHz	1670.858(4)	1652.52(1)
C/MHz	1257.385(3)	1255.20(1)
D_J/kHz	-0.00102(3)	1.4(3)
D_{JK}/kHz	-0.0118(2)	17(4)
d_1/kHz	-0.00032(3)	-1.0(2)
d_2/kHz	-0.00010(2)	-2.5(2)
σ/kHz	11.613	12.356
N	18	9

Table S11: Experimental rotational parameters of the parent and deuterated species of **D2W2**. The labelling of the atoms follows the ones displayed in Table S7. The error in parenthesis are in unit of the last digit. σ is the root-mean-square deviation of the fit. N is the number of the fitted transitions.

D2W2	Parent	$(D_2O)_2$	D13	D14
A/MHz	1759.4166(4)	1647.496(6)	1718.01(4)	1740.27(8)
B/MHz	763.3093(1)	749.7242(4)	760.059(1)	759.149(3)
C/MHz	696.9655(1)	684.3170(4)	692.471(1)	693.657(1)
D_J/kHz	0.6998(7)	0.598(2)	0.653(5)	0.65(1)
D_{JK}/kHz	-1.892(6)	-1.24(2)	-1.47(6)	-1.6(1)
D_K/kHz	10.66(3)	4(1)		
d_1/kHz	-0.1309(5)	-0.103(1)	-0.115(6)	-0.11(1)
d_2/kHz	0.0013(3)	0.006(1)		
σ/kHz	5.787	13.037	7.477	9.636
N	158	69	23	18

D2W2	D13,14	D13,14,16
A/MHz	1699.7(1)	1665.57(5)
B/MHz	756.110(1)	751.785(1)
C/MHz	689.370(1)	685.028(1)
D_J/kHz	0.482(9)	0.636(5)
D_{JK}/kHz	-1.5(5)	-1.61(8)
d_1/kHz		-0.129(7)
d_2/kHz		
σ/kHz	12.026	7.436
N	13	20

Table S12: Experimental rotational parameters of the parent species of **DW3**. The error in parenthesis are in unit of the last digit. σ is the root-mean-square deviation of the fit. N is the number of the fitted transitions.

DW3	Parent
A/MHz	2755.9026(8)
B/MHz	1182.2330(5)
C/MHz	1105.3436(4)
D_J/kHz	1.019(4)
D_{JK}/kHz	8.70(1)
D_K/kHz	-5.73(4)
d_1/kHz	-0.033(3)
d_2/kHz	0.024(1)
σ/kHz	8.088
N	103

10] **EXPERIMENTAL** ROTATIONAL FREQUENCIES

Table S13: Measured rotational transition frequencies (ν_{obs}) the parent species of **D2W** and residual (ν_{obs}-ν_{calc}) for the fit of Table S9 (frequencies in MHz).

J'	K_a'	K_c'	J"	K_a"	K_c"	v=0		v=1	
						ν_{obs}	ν_{obs}-ν_{calc}	ν_{obs}	ν_{obs}-ν_{calc}
μ_a-type transitions									
2	0	2	1	0	1	3881.3803	0.0047	3881.2792	0.0012
2	1	2	1	1	1	3677.9730	0.0037	3677.8236	0.0005
2	1	1	1	1	0	4149.8660	0.0167	4149.8105	-0.0173
3	0	3	2	0	2	5744.1496	0.0037	5743.9693	-0.0008
3	1	3	2	1	2	5497.6330	0.0027	5497.4023	-0.0014
3	1	2	2	1	1	6202.5777	0.0132	6202.5777	0.0547
3	2	2	2	2	1	5869.9782	0.0030	5869.8556	0.0002
3	2	1	2	2	0	5996.9226	0.0043	5996.8433	-0.0011
4	0	4	3	0	3	7532.6041	0.0012	7532.3241	-0.0016
4	1	4	3	1	3	7297.8443	0.0012	7297.5283	-0.0013
4	1	3	3	1	2	8224.5130	-0.0152	8224.5130	0.0588
4	2	3	3	2	2	7800.7214	0.0006	7800.5545	0.0018
4	2	2	3	2	1	8095.9144	-0.0126	8095.9144	0.0546
4	3	2	3	3	1	7882.6141	-0.0034	7882.4862	-0.0033
4	3	1	3	3	0	7899.6609	-0.0001	7899.5226	-0.0177
5	0	5	4	0	4	9261.4269	0.0014	9261.0336	-0.0019
5	1	5	4	1	4	9077.5370	0.0013	9077.1277	-0.0013
5	1	4	4	1	3	10199.1070	-0.0009	10198.9621	-0.0214
5	2	4	4	2	3	9709.6952	-0.0034	9709.4715	-0.0046
5	2	3	4	2	2	10231.4584	-0.0102	10231.4584	0.0483
5	3	3	4	3	2	9866.2383	-0.0090	9866.1000	0.0061
5	3	2	4	3	1	9924.2834	-0.0090	9924.1463	-0.0162
5	4	2	4	4	1	9850.7283	-0.0156	9850.5969	-0.0084
5	4	1	4	4	0	9852.3984	-0.0138	9852.2603	-0.0140
6	0	6	5	0	5	10962.0034	0.0023	10961.4985	-0.0009
6	1	6	5	1	5	10838.5496	-0.0010	10838.0455	-0.0006
6	1	5	5	1	4	12107.0499	-0.0165	12106.8628	-0.0068
6	2	5	5	2	4	11592.5748	-0.0023	11592.2917	-0.0020
6	2	4	5	2	3	12364.7567	-0.0164	12364.7567	0.0459
6	3	3	5	3	2	11994.1768	-0.0217	11994.0654	-0.0096
6	3	4	5	3	3	11847.3436	0.0047	11847.1814	0.0214
6	4	2	5	4	1	11849.5451	-0.0037	11849.3987	-0.0025
6	4	3	5	4	2	11842.1476	0.0025	11842.0108	0.0162
7	0	7	6	0	6	12658.7694	0.0070	12658.1574	0.0026
7	1	7	6	1	6	12584.5718	0.0039	12583.9759	0.0127
7	1	6	6	1	5	13933.5341	-0.0098	13933.2356	-0.0023
7	2	6	6	2	5	13446.4649	-0.0049	13446.1140	-0.0062
7	2	5	6	2	4	14461.7840	-0.0315	14461.7840	0.0530
7	3	5	6	3	4	13818.0151	-0.0005	13817.8148	0.0052
7	3	4	6	3	3	14119.5982	-0.0586	14119.5982	0.0450
7	4	4	6	4	3	13841.8455	0.0056	13841.6884	0.0046
7	4	3	6	4	2	13865.9354	0.0025	13865.7808	-0.0047
8	0	8	7	0	7	14361.1450	0.0013	14360.4366	0.0021
8	1	8	7	1	7	14319.7655	-0.0045	14319.0669	0.0021
8	1	7	7	1	6	15680.4595	-0.0213	15680.0932	-0.0015
8	2	7	7	2	6	15270.5502	-0.0035	15270.1300	-0.0055
8	2	6	7	2	5	16500.2240	-0.0803	16500.2240	0.0439
8	3	6	7	3	5	15770.1286	0.0198	15769.8835	0.0097
8	3	5	7	3	4	16293.6128	-0.0074	16293.5346	-0.0040
8	4	5	7	4	4	15847.1412	0.0169	15846.9713	0.0044
9	0	9	8	0	8	16069.7447	-0.0152	16068.9445	-0.0081
9	1	9	8	1	8	16047.8644	0.0320	16047.0344	0.0065
9	1	8	8	1	7	17372.3637	-0.0014	17371.8769	-0.0146
9	2	8	8	2	7	17066.3674	-0.0033	17065.8940	0.0083
9	3	7	8	3	6	17696.4808	0.0175	17696.2072	0.0077
10	0	10	9	0	9	17782.7005	0.0074	17781.7971	0.0057
10	1	10	9	1	9	17771.4636	-0.0185	17770.5745	-0.0068

μ_b-type transitions									
3	1	3	2	0	2	6445.7093	-0.0032	6445.6041	0.0260
4	1	4	3	0	3	7999.4162	0.0067	7999.1308	-0.0068
5	1	5	4	0	4	9544.3486	0.0063	9543.9424	0.0015
6	1	6	5	0	5	11121.4715	0.0041		
7	1	7	6	0	6	12744.0370	0.0028		
4	0	4	3	1	3	6831.0343	-0.0022	6830.7270	0.0093
5	0	5	4	1	4	8794.6152	-0.0037	8794.2244	0.0008
6	0	6	5	1	5	10679.0758	-0.0085	10678.5909	-0.0030
7	0	7	6	1	6	12499.2955	-0.0007	12498.6977	-0.0049

Table S14: Measured rotational transition frequencies (ν_{obs}) for the isotopologue of **DW2** with full deuterated (DFM2-D_2O) water and residual (ν_{obs}-ν_{calc}) for the fit of table S10 (frequencies in MHz).

J'	K_a'	K_c'	J"	K_a"	K_c"	ν_{obs}	ν_{obs}-ν_{calc}
4	0	4	3	0	3	7418.7487	-0.0343
4	1	4	3	1	3	7201.3376	-0.0432
4	1	3	3	1	2	8160.6195	0.0016
4	2	2	3	2	1	8070.1305	0.0024
4	2	3	3	2	2	7726.7015	0.0104
4	3	2	3	3	1	7821.9167	0.0041
4	3	1	3	3	0	7845.4183	-0.0035
5	0	5	4	0	4	9108.2720	-0.0104
5	1	4	4	1	3	10099.2206	0.0026
5	1	5	4	1	4	8950.2476	-0.0259
5	2	3	4	2	2	10200.3787	-0.0032
5	2	4	4	2	3	9608.1553	0.0287
5	3	3	4	3	2	9789.3919	-0.0063
5	3	2	4	3	1	9868.7922	-0.0177
6	0	6	5	0	5	10777.1455	0.0257
6	1	5	5	1	4	11955.4435	0.0052
6	1	6	5	1	5	10679.2543	0.0021
6	2	4	5	2	3	12313.0215	-0.0166
6	2	5	5	2	4	11458.1930	0.0416
6	3	4	5	3	3	11750.4012	-0.0052
6	3	3	5	3	2	11947.9361	-0.0063
7	0	7	6	0	6	12447.5271	0.0108
7	1	6	6	1	5	13717.2030	-0.0162
7	1	7	6	1	6	12393.1815	0.0159
7	2	5	6	2	4	14372.5975	0.0093
7	2	6	6	2	5	13274.0392	0.0281
7	3	5	6	3	4	13694.8508	-0.0027
7	3	4	6	3	3	14088.9242	0.0147
8	0	8	7	0	7	14125.0263	0.0285
8	1	8	7	1	7	14096.9106	0.0067
8	2	6	7	2	5	16355.4965	0.0013
8	2	7	7	2	6	15055.8393	-0.0467
8	3	5	7	3	4	16269.8347	-0.0065
8	3	6	7	3	5	15613.0021	0.0121
9	1	9	8	1	8	15794.3254	-0.0231
9	0	9	8	0	8	15808.1781	-0.0044

Table S15: Measured rotational transition frequencies (ν_{obs}) for the isotopologue of **D2W** – D12 and residual (ν_{obs}-ν_{calc}) for the fit of table S9 (frequencies in MHz).

J'	K_a'	K_c'	J"	K_a"	K_c"	ν_{obs}	ν_{obs}-ν_{calc}
4	0	4	3	0	3	7507.0156	0.0071
4	1	3	3	1	2	8214.2826	0.0100
4	1	4	3	1	3	7276.9844	0.0106
4	2	2	3	2	1	8096.2869	0.0130
4	2	3	3	2	2	7786.9691	0.0050
4	3	2	3	3	1	7872.6475	-0.0199

4	3	1	3	3	0	7891.4227	-0.0209
5	0	5	4	0	4	9225.8275	0.0030
5	1	4	4	1	3	10180.7371	0.0055
5	1	5	4	1	4	9049.4887	0.0067
5	2	3	4	2	2	10232.8239	0.0126
5	2	4	4	2	3	9690.0247	0.0272
5	3	3	4	3	2	9853.6896	0.0078
5	3	2	4	3	1	9917.4847	-0.0028
5	4	2	4	4	1	9837.4916	-0.0304
6	0	6	5	0	5	10918.5266	-0.0042
6	1	5	5	1	4	12076.0667	-0.0200
6	1	6	5	1	5	10802.9077	0.0086
6	2	4	5	2	3	12362.8381	-0.0098
6	2	5	5	2	4	11565.4404	-0.0012
6	3	3	5	3	2	11991.8438	-0.0109
6	3	4	5	3	3	11831.1694	0.0140
6	4	2	5	4	1	11835.5988	0.0050
6	4	3	5	4	2	11827.0603	0.0016
7	0	7	6	0	6	12609.1489	0.0071
7	1	6	6	1	5	13885.8502	-0.0503
7	1	7	6	1	6	12541.2188	-0.0237
7	2	5	6	2	4	14451.8035	-0.0054
7	2	6	6	2	5	13410.3876	-0.0314
7	3	5	6	3	4	13796.5885	0.0002
7	3	4	6	3	3	14124.0427	0.0079
7	4	4	6	4	3	13824.8755	0.0212
7	4	3	6	4	2	13852.5670	-0.0161
8	0	8	7	0	7	14305.9465	0.0046
8	1	7	7	1	6	15615.4096	0.0126
8	1	8	7	1	7	14268.9182	0.0038
8	2	6	7	2	5	16477.1816	0.0035
8	2	7	7	2	6	15224.3581	0.0062
8	3	6	7	3	5	15741.3502	0.0060
8	4	5	7	4	4	15827.7031	0.0272
8	4	4	7	4	3	15900.7553	-0.0118
9	0	9	8	0	8	16008.8706	-0.0019
9	1	8	8	1	7	17293.3003	0.0086
9	1	9	8	1	8	15989.6652	-0.0024
4	1	4	3	0	3	7941.5973	0.0027
3	1	3	2	0	2	6393.4258	0.0059
4	0	4	3	1	3	6842.3994	0.0118
2	2	1	1	1	0	7491.8827	-0.0096
2	2	0	1	1	1	7765.4785	0.0212
5	0	5	4	1	4	8791.2525	0.0141
3	2	2	2	1	1	9205.6376	-0.0005
5	1	5	4	0	4	9484.0800	0.0118
6	0	6	5	1	5	10660.2702	-0.0170
4	2	3	3	1	2	10795.5015	-0.0075
6	1	6	5	0	5	11061.1475	0.0047
3	3	1	2	2	0	12019.0151	-0.0140
3	3	0	2	2	1	12056.7600	0.0208
4	3	2	3	2	1	13897.1504	-0.0083
4	3	1	3	2	2	14087.3316	0.0008

Table S16: Measured rotational transition frequencies (ν_{obs}) for the isotopologue of **D2W**-D13 and residual (ν_{obs}-ν_{calc}) for the fit of table S9 (frequencies in MHz).

J'	K_a'	K_c'	J"	K_a"	K_c"	ν_{obs}	ν_{obs}-ν_{calc}
4	0	4	3	0	3	7430.4700	0.0070
4	1	4	3	1	3	7208.2922	-0.0003
4	1	3	3	1	2	8167.1048	-0.0034
4	2	3	3	2	2	7733.1157	-0.0035
4	2	2	3	2	1	8068.2034	0.0071
4	3	2	3	3	1	7826.6063	0.0321

4	3	1	3	3	0	7848.6679	0.0073
5	0	5	4	0	4	9124.1643	0.0101
5	1	5	4	1	4	8960.2080	0.0014
5	1	4	4	1	3	10111.5710	-0.0012
5	2	4	4	2	3	9618.3722	-0.0074
5	2	3	4	2	2	10198.9653	0.0060
5	3	2	4	3	1	9870.7634	0.0078
5	3	3	4	3	2	9796.0341	-0.0113
6	0	6	5	0	5	10795.6402	0.0120
6	1	6	5	1	5	10692.4141	-0.0047
6	1	5	5	1	4	11977.0058	-0.0079
6	2	5	5	2	4	11473.5602	-0.0034
6	2	4	5	2	3	12315.5504	-0.0136
6	3	3	5	3	2	11946.6948	-0.0395
6	3	4	5	3	3	11760.2873	0.0066
7	0	7	6	0	6	12467.7738	-0.0186
7	1	7	6	1	6	12409.5346	-0.0181
7	1	6	6	1	5	13750.5873	-0.0019
7	2	6	6	2	5	13295.9202	0.0036
7	2	5	6	2	4	14382.8115	0.0181
7	3	5	6	3	4	13709.7289	-0.0088
7	3	4	6	3	3	14083.9035	0.0115
8	0	8	7	0	7	14146.9628	0.0162
8	1	8	7	1	7	14116.3750	0.0012
8	1	7	7	1	6	15444.2531	-0.0082
8	2	7	7	2	6	15085.4322	0.0144

Table S17: Measured rotational transition frequencies (ν_{obs}) of parent species of **DW2** and residual (ν_{obs}-ν_{calc}) for the fit of table S10 (frequencies in MHz).

J'	K_a'	K_c'	J"	K_a"	K_c"	v=0		v=1	
						ν_{obs}	ν_{obs}-ν_{calc}	ν_{obs}	ν_{obs}-ν_{calc}
1	0	1	0	0	0	3045.7369	0.0061	3045.8221	0.0032
2	1	2	1	1	1	5678.0543	0.0035	5678.1127	0.0305
2	0	2	1	0	1	6057.1325	0.0034	6057.2857	0.0030
2	1	1	1	1	0	6504.7026	-0.0091	6505.0248	-0.0070
3	1	3	2	1	2	8496.4189	0.0128	8496.4189	-0.0327
3	0	3	2	0	2	9001.4137	0.0035	9001.5925	0.0039
3	2	2	2	2	1	9136.7874	0.0043	9137.0471	0.0058
3	2	1	2	2	0	9272.4220	0.0017	9272.7632	-0.0081
3	1	2	2	1	1	9734.5536	-0.0091	9735.0229	-0.0011
4	1	4	3	1	3	11292.3998	0.0294	11292.3998	-0.0321
4	0	4	3	0	3	11852.9800	0.0042	11853.1371	0.0036
4	2	3	3	2	2	12155.5300	0.0121	12155.8615	0.0067
4	3	2	3	3	1	12245.2879	0.0001	12245.6714	0.0125
4	3	1	3	3	0	12255.9457	-0.0057	12256.3420	0.0085
4	2	2	3	2	1	12485.0314	0.0054	12485.5621	-0.0119
4	1	3	3	1	2	12934.8601	-0.0105	12935.4613	0.0118
5	1	5	4	1	4	14062.2463	0.0194	14062.2463	-0.0666
5	0	5	4	0	4	14603.4932	0.0031	14603.5600	-0.0416
5	2	4	4	2	3	15151.4197	0.0094	15151.8027	-0.0194
5	3	3	4	3	2	15327.1889	-0.0032	15327.5549	-0.0255
5	3	2	4	3	1	15364.1501	-0.0060	15364.5945	0.0219
5	2	3	4	2	2	15775.2486	0.0133	15775.9892	-0.0179
5	1	4	4	1	3	16091.5586	-0.0077	16092.2558	0.0251
6	1	6	5	1	5	16804.8633	0.0172	16804.9759	0.0007
6	0	6	5	0	5	17268.5342	-0.0163	17268.6618	0.0299

Table S18: Measured rotational transition frequencies (ν_{obs}) of **DW2** with full deuterated water (DFM-$(D_2O)_2$) and residual (ν_{obs}-ν_{calc}) for the fit of table S10 (frequencies in MHz).

J'	K_a'	K_c'	J"	K_a"	K_c"	v=0		v=1	
						ν_{obs}	ν_{obs}-ν_{calc}	ν_{obs}	ν_{obs}-ν_{calc}
3	1	3	2	1	2	7935.4897	-0.0278	7935.4897	0.0630
3	0	3	2	0	2	8416.5153	-0.0057	8416.4212	-0.0124
3	2	2	2	2	1	8562.6103	-0.0247	8562.6103	0.0561
3	2	1	2	2	0	8708.9955	-0.0016	8708.8897	-0.0267
3	1	2	2	1	1	9143.5598	-0.0048	9143.4890	0.0014
4	1	4	3	1	3	10541.9924	-0.0263	10541.8989	-0.0123
4	0	4	3	0	3	11063.5502	0.0136	11063.3995	-0.0260
4	1	3	3	1	2	12142.7553	-0.0064	12142.6583	0.0076
4	2	3	3	2	2	11387.7885	-0.0260	11387.7885	0.0779
4	2	2	3	2	1	11741.2127	-0.0162	11741.0986	-0.0192
5	1	5	4	1	4	13121.1738	0.0038	13121.0704	0.0109
5	0	5	4	0	4	13608.1835	-0.0094	13608.0792	0.0063
5	2	4	4	2	3	14188.3721	0.0283	14188.2791	0.0565
5	3	3	4	3	2	14376.7221	-0.0039	14376.6062	0.0109
5	3	2	4	3	1	14420.9526	-0.0054	14420.8060	-0.0158
5	2	3	4	2	2	14850.4676	0.0168	14850.3141	0.0156
5	1	4	4	1	3	15093.7536	-0.0048	15093.6111	0.0002
6	1	6	5	1	5	15672.4055	0.0014	15672.3088	-0.0010
6	0	6	5	0	5	16072.8409	0.0056	16072.7356	0.0054
6	2	5	5	2	4	16958.6261	-0.0158	16958.4732	-0.0399

Table S19: Measured rotational transition frequencies (ν_{obs}) for the D8 isotopologue of **DW2** and residual (ν_{obs}-ν_{calc}) for the fit of table S10 (frequencies in MHz).

J'	K_a'	K_c'	J"	K_a"	K_c"	v=0		v=1	
						ν_{obs}	ν_{obs}-ν_{calc}	ν_{obs}	ν_{obs}-ν_{calc}
2	1	1	1	1	0	6386.7264	0.0527		
3	1	3	2	1	2	8302.5528	0.0062		
3	0	3	2	0	2	8804.4863	-0.0018	8804.6669	-0.0132
3	2	2	2	2	1	8952.2323	-0.0106	8952.4998	-0.0151
3	1	2	2	1	1	9555.3005	-0.0308		
4	1	4	3	1	3	11030.8727	0.0041	11030.87268	0.0041
4	0	4	3	0	3	11578.4018	-0.0200	11578.5951	0.0027
4	2	3	3	2	2	11906.9512	-0.0306	11907.3400	0.0254
4	1	3	3	1	2	12691.3618	-0.0110	12691.9646	0.0036
5	1	5	4	1	4	13731.3383	0.0103		
5	0	5	4	0	4	14247.1018	0.0216	14247.6802	0.0016
5	2	4	4	2	3	14836.8174	0.0191	14837.2323	-0.0128
5	2	3	4	2	2	15509.3859	-0.0076		
5	1	4	4	1	3	15778.9612	0.0051	15778.02976	0.0
6	1	6	5	1	5	16403.1757	-0.0141		
4	2	2	3	2	1	12265.0441	0.0237		

Table S20: Measured rotational transition frequencies (ν_{obs}) for the D9 isotopologue of **DW2** and residual (ν_{obs}-ν_{calc}) for the fit of table S10 (frequencies in MHz).

J'	K_a'	K_c'	J"	K_a"	K_c"	v=0		v=1	
						ν_{obs}	ν_{obs}-ν_{calc}	ν_{obs}	ν_{obs}-ν_{calc}
2	1	1	1	1	0	6415.2987	-0.0024	6415.6309	-0.0115
3	1	3	2	1	2	8388.0802	-0.0006	8388.2886	-0.0202
3	0	3	2	0	2	8884.7806	-0.0068	8885.0202	-0.0245
3	2	2	2	2	1	9015.1854	0.0460	9015.4556	-0.0015
3	2	1	2	2	0	9145.8743	0.0178	9146.2242	-0.0070
3	1	2	2	1	1	9601.2957	-0.0070	9601.7885	-0.0032
4	1	4	3	1	3	11149.2175	-0.0007	11149.6604	0.0385
4	0	4	3	0	3	11702.6156	-0.0191	11702.9272	0.0114
4	2	3	3	2	2	11994.2704	-0.0426	11994.8511	0.0029

4	2	2	3	2	1	12312.1315	-0.0266	12312.7866	0.0020
5	1	5	4	1	4	13885.1162	0.0204	13885.7544	-0.0152
4	1	3	3	1	2	12758.9165	-0.0037	12759.5765	0.0359
5	0	5	4	0	4	14422.1979	-0.0031		
6	1	6	5	1	5	16594.5330	-0.0032		
5	1	4	4	1	3	15874.7110	0.0250	15875.4189	-0.0187
5	2	3	4	2	2	15554.2028	-0.0132	15555.0881	0.0014

Table S21: Measured rotational transition frequencies (ν_{obs}) for the D11 isotopologue of **DW2** and residual (ν_{obs}-ν_{calc}) for the fit of table S10 (frequencies in MHz).

J'	K_a'	K_c'	J"	K_a"	K_c"	v=0		v=1	
						ν_{obs}	ν_{obs}-ν_{calc}	ν_{obs}	ν_{obs}-ν_{calc}
2	1	1	1	1	0	6468.9515	-0.0398	6469.0739	0.0121
3	1	3	2	1	2	8431.9309	0.0076	8431.9308	-0.0099
3	0	3	2	0	2	8936.9757	0.0024	8936.9756	-0.0049
3	2	2	2	2	1	9078.2130	0.0067	9078.2130	-0.0307
3	2	1	2	2	0	9219.6867	0.0078		
3	1	2	2	1	1	9679.9623	0.0016	9679.9624	-0.0297
4	1	4	3	1	3	11204.9426	-0.0048		
4	0	4	3	0	3	11761.3196	0.0013	11761.3196	-0.0239
4	1	3	3	1	2	12859.9866	0.0314	12859.9866	0.0358
4	2	2	3	2	1	12419.2432	-0.0052	12419.4933	0.0027
4	2	3	3	2	2	12076.2700	0.0161	12076.2700	-0.0164
5	1	5	4	1	4	13950.9928	-0.0065	13951.1067	0.0082
5	0	5	4	0	4	14482.3538	-0.0092	14482.4673	0.0401
5	2	4	4	2	3	15050.4449	-0.0043	15050.4896	-0.0096
5	2	3	4	2	2	15697.6400	-0.0066		
5	1	4	4	1	3	15994.0877	-0.0061	15994.2092	-0.0142
6	1	6	5	1	5	16669.1771	0.0063	16669.3021	-0.0025
6	0	6	5	0	5			17118.2330	-0.0182

Table S22: Measured rotational transition frequencies (ν_{obs}) for the D8,9 isotopologue of **DW2** and residual (ν_{obs}-ν_{calc}) for the fit of table S10 (frequencies in MHz).

J'	K_a'	K_c'	J"	K_a"	K_c"	v=0		v=1	
						ν_{obs}	ν_{obs}-ν_{calc}	ν_{obs}	ν_{obs}-ν_{calc}
3	1	3	2	1	2	8200.4489	-0.0070	8200.4489	-0.0202
3	0	3	2	0	2	8694.1581	0.0096	8694.3550	0.0111
3	1	2	2	1	1	9426.5780	0.0027	9427.0562	-0.0060
3	2	1	2	2	0	8977.8286	0.0125		
3	2	2	2	2	1	8835.8355	-0.0035	8836.1260	0.0381
4	1	4	3	1	3	10896.2758	0.0052	10896.2758	-0.0299
4	0	4	3	0	3	11437.4499	0.0039	11437.6379	0.0222
4	1	3	3	1	2	12521.8247	-0.0066	12522.4482	0.0093
4	2	3	3	2	2	11752.9828	-0.0048	11753.4419	-0.0076
4	2	2	3	2	1	12096.7879	-0.0063	12096.8899	-0.0479
5	1	5	4	1	4	13565.1879	-0.0016	13565.2943	0.0482
5	0	5	4	0	4	14078.4399	0.0047	14078.5381	-0.0094
5	1	4	4	1	3	15570.8459	0.0034	15571.5737	-0.0131
5	2	4	4	2	3	14646.2359	0.0032		
5	2	3	4	2	2	15293.4976	-0.0038	15293.6195	0.0274
5	3	3	4	3	2	14829.4266	-0.0088		
5	3	2	4	3	1	14870.3959	0.0113		
6	1	6	5	1	5	16206.3739	-0.0008		
6	0	6	5	0	5			16636.4601	-0.0158

Table S23: Measured rotational transition frequencies (ν_{obs}) for the D8,11 isotopologue of **DW2** and residual (ν_{obs}-ν_{calc}) for the fit of table S10 (frequencies in MHz).

J'	K_a'	K_c'	J"	K_a"	K_c"	ν_{obs}	ν_{obs}-ν_{calc}
3	1	3	2	1	2	8241.7102	0.0054
3	0	3	2	0	2	8743.6160	0.0046
3	2	2	2	2	1	8898.2486	0.0129
3	2	1	2	2	0	9053.1344	0.0140
3	1	2	2	1	1	9505.8797	-0.0037
4	1	4	3	1	3	10948.0638	-0.0042
4	0	4	3	0	3	11490.6843	-0.0145
4	2	3	3	2	2	11833.5681	-0.0072
4	2	2	3	2	1	12207.2271	-0.0334
4	1	3	3	1	2	12622.9291	-0.0027
5	1	5	4	1	4	13625.6068	0.0098
5	0	5	4	0	4	14130.2701	-0.0009
5	2	4	4	2	3	14742.8854	0.0070
5	2	3	4	2	2	15442.0854	-0.0051
5	1	4	4	1	3	15688.8339	0.0089
6	1	6	5	1	5	16273.7662	-0.0053
6	0	6	5	0	5	16686.7362	0.0033

Table S24: Measured rotational transition frequencies (ν_{obs}) for the D9,11 isotopologue of **DW2** and residual (ν_{obs}-ν_{calc}) for the fit of table S10 (frequencies in MHz).

J'	K_a'	K_c'	J"	K_a"	K_c"	ν_{obs}	ν_{obs}-ν_{calc}
2	1	1	1	1	0	6381.6397	-0.0003
3	1	3	2	1	2	8325.9507	0.0038
3	0	3	2	0	2	8823.0113	-0.0016
3	2	2	2	2	1	8959.3221	-0.0029
3	2	1	2	2	0	9095.9203	0.0038
3	1	2	2	1	1	9549.7791	-0.0057
4	1	4	3	1	3	11064.9013	-0.0073
4	0	4	3	0	3	11614.4242	-0.0166
4	2	3	3	2	2	11918.7259	0.0093
4	2	2	3	2	1	12250.2027	0.0151
4	1	3	3	1	2	12688.1177	0.0063
5	1	5	4	1	4	13777.7431	0.0174
5	0	5	4	0	4	14305.1626	-0.0109
5	2	4	4	2	3	14855.1130	0.0136
5	2	3	4	2	2	15481.5380	-0.0164
5	1	4	4	1	3	15782.3607	0.0152
6	1	6	5	1	5	16463.3778	0.0038
6	0	6	5	0	5	16911.9959	-0.0104

Table S25: Measured rotational transition frequencies (ν_{obs}) for the D10,11 isotopologue of **DW2** and residual (ν_{obs}-ν_{calc}) for the fit of table S10 (frequencies in MHz).

J'	K_a'	K_c'	J"	K_a"	K_c"	ν_{obs}	ν_{obs}-ν_{calc}
3	1	3	2	1	2	8203.9190	-0.0235
3	0	3	2	0	2	8694.3550	0.0266
3	2	2	2	2	1	8831.0361	0.0114
3	2	1	2	2	0	8968.0681	-0.0108
3	1	2	2	1	1	9415.1225	-0.0126
4	1	4	3	1	3	10902.0834	0.0233
4	0	4	3	0	3	11442.2298	-0.0245
4	1	3	3	1	2	12507.2383	0.0129
5	1	5	4	1	4	13574.0674	-0.0048
5	0	5	4	0	4	14090.1053	0.0039
5	1	4	4	1	3	15554.1418	-0.0032

Table S26: Measured rotational transition frequencies (ν_{obs}) for the D8,9,11 isotopologue of **DW2** and residual (ν_{obs}-ν_{calc}) for the fit of table S10 (frequencies in MHz).

J'	K_a'	K_c'	J"	K_a"	K_c"	ν_{obs}	ν_{obs}-ν_{calc}
3	1	3	2	1	2	8141.7909	0.0048
3	0	3	2	0	2	8635.7818	0.0057
3	2	1	2	2	0	8933.1747	0.0026
3	2	2	2	2	1	8784.3479	0.0014
3	1	2	2	1	1	9379.9868	0.0135
4	1	4	3	1	3	10816.3752	0.0025
4	0	4	3	0	3	11352.9954	-0.0214
4	2	3	3	2	2	11682.9321	-0.0274
4	3	1	3	3	0	11794.1485	0.0134
4	2	2	3	2	1	12042.4857	-0.0184
4	1	3	3	1	2	12457.2067	0.0016
5	1	5	4	1	4	13463.1032	0.0140
5	0	5	4	0	4	13965.6216	0.0060
5	2	4	4	2	3	14556.5232	0.0024
5	2	3	4	2	2	15230.6935	-0.0018
5	1	4	4	1	3	15485.5355	0.0103
6	1	6	5	1	5	16081.3097	0.0022
6	0	6	5	0	5	16495.8651	-0.0089

Table S27: Measured rotational transition frequencies (ν_{obs}) for the D9,10,11 isotopologue of **DW2** and residual (ν_{obs}-ν_{calc}) for the fit of table S10 (frequencies in MHz).

J'	K_a'	K_c'	J"	K_a"	K_c"	ν_{obs}	ν_{obs}-ν_{calc}
3	1	3	2	1	2	8106.8365	0.0260
3	0	3	2	0	2	8589.9000	-0.0223
3	1	2	2	1	1	9296.7908	-0.0483
4	1	4	3	1	3	10773.7238	0.0359
4	0	4	3	0	3	11307.4916	0.0081
4	2	3	3	2	2	11604.3723	-0.0028
4	2	2	3	2	1	11926.1410	-0.0039
4	1	3	3	1	2	12351.9058	0.0037
5	1	5	4	1	4	13415.0629	-0.0228
5	0	5	4	0	4	13927.0519	-0.0355
5	1	4	4	1	3	15364.0329	0.0038
6	0	6	5	0	5	16465.0772	0.0199

Table S28: Measured rotational transition frequencies (ν_{obs}) for the parent species of **D2W2** and residual (ν_{obs}-ν_{calc}) for the fit of table S11 (frequencies in MHz).

J'	K_a'	K_c'	J"	K_a"	K_c"	ν_{obs}	ν_{obs}-ν_{calc}
2	1	2	1	1	1	2854.1958	0.0004
2	0	2	1	0	1	2917.3231	0.0002
2	1	1	1	1	0	2986.8750	0.0004
3	0	3	2	0	2	4367.9785	-0.0038
3	1	3	2	1	2	4279.3003	-0.0021
3	1	2	2	1	1	4478.2051	-0.0036
3	2	1	2	2	0	4393.5755	0.0139
3	2	2	2	2	1	4380.8131	0.0187
4	0	4	3	0	3	5809.3230	-0.0035
4	1	4	3	1	3	5702.1519	-0.0029
4	1	3	3	1	2	5966.8793	-0.0033
4	2	3	3	2	2	5838.4841	-0.0029
4	2	2	3	2	1	5870.0758	-0.0034
4	3	2	3	3	1	5847.1977	0.0142
4	3	1	3	3	0	5847.7656	0.0018
5	0	5	4	0	4	7239.1106	-0.0019
5	1	5	4	1	4	7122.2159	-0.0008

5	1	4	4	1	3	7451.7770	-0.0040
5	2	3	4	2	2	7355.8730	-0.0032
5	2	4	4	2	3	7293.9802	-0.0020
5	3	2	4	3	1	7313.2438	-0.0007
5	3	3	4	3	2	7311.2204	-0.0003
5	4	1	4	4	0	7308.4621	-0.0022
5	4	2	4	4	1	7308.4578	0.0129
6	0	6	5	0	5	8656.3842	-0.0011
6	1	6	5	1	5	8539.1199	0.0000
6	1	5	5	1	4	8931.5912	-0.0012
6	1	5	5	1	4	8931.5907	-0.0017
6	2	5	5	2	4	8746.7445	-0.0021
6	2	4	5	2	3	8851.3211	-0.0002
6	3	4	5	3	3	8776.2626	0.0006
6	3	3	5	3	2	8781.6244	-0.0010
6	4	3	5	4	2	8772.3034	0.0355
6	4	2	5	4	1	8772.3034	-0.0517
6	5	2	5	5	1	8769.6377	0.0085
6	5	1	5	5	0	8769.6377	0.0080
7	0	7	6	0	6	10061.9376	-0.0012
7	1	7	6	1	6	9952.6755	-0.0034
7	1	6	6	1	5	10404.7758	-0.0022
7	2	6	6	2	5	10196.2694	0.0011
7	2	5	6	2	4	10355.0075	-0.0004
7	3	5	6	3	4	10242.0650	0.0013
7	3	4	6	3	3	10254.0075	-0.0013
7	4	4	6	4	3	10237.2080	-0.0022
7	4	3	6	4	2	10237.5023	0.0027
7	5	3	6	5	2	10233.0036	0.0037
7	5	2	6	5	1	10233.0036	0.0007
8	0	8	7	0	7	11458.2013	0.0038
8	1	8	7	1	7	11362.8963	0.0059
8	1	7	7	1	6	11869.5758	-0.0006
8	2	7	7	2	6	11642.0724	0.0014
8	2	6	7	2	5	11863.8611	0.0081
8	3	6	7	3	5	11708.2025	0.0007
8	3	5	7	3	4	11731.7241	0.0063
8	4	5	7	4	4	11703.4028	0.0065
8	4	4	7	4	3	11704.1971	0.0088
8	5	4	7	5	3	11697.2050	0.0210
8	5	3	7	5	2	11697.2050	0.0089
9	0	9	8	0	8	12848.4249	0.0068
9	1	9	8	1	8	12769.9138	0.0028
9	1	8	8	1	7	13324.0961	0.0072
9	2	8	8	2	7	13083.7241	-0.0081
9	2	7	8	2	6	13373.8696	0.0014
9	3	7	8	3	6	13174.0912	-0.0035
9	3	6	8	3	5	13216.2142	0.0059
9	4	6	8	4	5	13170.8982	0.0006
9	4	5	8	4	4	13172.7824	-0.0020
10	0	10	9	0	9	14235.6606	-0.0038
10	1	10	9	1	9	14174.0173	-0.0040
10	1	9	9	1	8	14766.4882	-0.0053
10	2	9	9	2	8	14520.9042	0.0001
10	2	8	9	2	7	14881.1469	-0.0048
10	3	8	9	3	7	14639.0525	0.0109
10	3	7	9	3	6	14708.8505	-0.0006
11	0	11	10	0	10	15622.1426	-0.0007
11	1	11	10	1	10	15575.5787	-0.0016
11	1	10	10	1	9	16195.4178	-0.0033
3	1	3	2	0	2	5212.2750	-0.0009
4	1	4	3	0	3	6546.4436	-0.0048
5	1	5	4	0	4	7859.3373	-0.0014
6	1	6	5	0	5	9159.3459	-0.0001
7	1	7	6	0	6	10455.6416	0.0019

8	1	8	7	0	7	11756.6001	0.0088
9	1	9	8	0	8	13068.2964	-0.0084
4	0	4	3	1	3	4965.0359	0.0030
5	0	5	4	1	4	6501.9862	-0.0045
6	0	6	5	1	5	8036.1557	-0.0034
7	0	7	6	1	6	9558.9761	-0.0018
8	0	8	7	1	7	11064.4995	0.0029
9	0	9	8	1	8	12550.0412	0.0169
2	2	1	1	1	0	5975.0731	-0.0023
2	2	0	1	1	1	6044.6224	-0.0003
3	2	1	2	1	2	7583.9850	-0.0039
3	2	2	2	1	1	7368.9905	-0.0047
4	2	3	3	1	2	8729.2729	-0.0008
4	2	2	3	1	3	9174.7658	0.0000
5	2	4	4	1	3	10056.3736	0.0004
5	2	3	4	1	4	10828.4840	-0.0032
6	2	5	5	1	4	11351.3367	-0.0022
6	2	4	5	1	5	12557.5956	0.0039
7	2	6	6	1	5	12616.0215	0.0068
8	2	7	7	1	6	13853.3127	0.0050
3	3	0	2	2	1	9528.6671	0.0025
3	3	1	2	2	0	9525.3661	0.0030
4	3	2	3	2	1	10978.9857	0.0007
4	3	1	3	2	2	10995.6394	0.0055
5	3	3	4	2	2	12420.1325	0.0061
5	3	2	4	2	3	12470.3920	0.0007
6	3	4	5	2	3	13840.4976	-0.0146
6	3	3	5	2	4	13958.0345	0.0000
7	3	4	6	2	5	15465.2945	-0.0023
7	3	5	6	2	4	15231.2389	-0.0157
8	3	5	7	2	6	17000.7444	-0.0019
8	3	6	7	2	5	16584.4323	-0.0162
3	1	2	2	0	2	5610.2032	-0.0009
4	1	3	3	0	3	7209.1019	-0.0026
5	1	4	4	0	4	8851.5552	-0.0037
6	1	5	5	0	5	10544.0316	-0.0073
7	1	6	6	0	6	12292.4298	-0.0018
8	1	7	7	0	7	14100.0616	-0.0077
9	1	8	8	0	8	15965.9751	0.0145
2	2	0	1	1	0	5978.2811	0.0012
2	2	1	1	1	1	6041.4176	-0.0006
3	2	1	2	1	1	7384.9667	-0.0002
3	2	2	2	1	2	7568.0259	0.0087
4	2	2	3	1	2	8776.8364	-0.0012
4	2	3	3	1	3	9127.2003	-0.0016
5	2	3	4	1	3	10165.8283	-0.0028
5	2	4	4	1	4	10719.0264	-0.0030
6	2	4	5	1	4	11565.3713	-0.0002
6	2	5	5	1	5	12343.5579	-0.0012
7	2	5	6	1	5	12988.7890	0.0020
7	2	6	6	1	6	14000.7013	-0.0063
8	2	6	7	1	6	14447.8573	-0.0047
9	2	7	8	1	7	15952.1416	-0.0122
3	3	0	2	2	0	9525.4699	0.0100
3	3	1	2	2	1	9528.5710	0.0033
4	3	1	3	2	1	10979.6684	0.0062
4	3	2	3	2	2	10994.9604	0.0036
5	3	2	4	2	2	12422.8352	0.0078
5	3	3	4	2	3	12467.6937	0.0034
6	3	3	5	2	3	13848.5747	-0.0019
6	3	4	5	2	4	13949.9748	0.0047
7	3	4	6	2	4	15251.2579	-0.0062
7	3	5	6	2	5	15445.2838	-0.0035
8	3	5	7	2	5	16627.9706	-0.0035
8	3	6	7	2	6	16957.2127	-0.0081

6	4	2	5	3	2	15964.6684	0.0045
6	4	3	5	3	3	15967.2485	-0.0074
7	4	3	6	3	3	17420.5340	-0.0042
7	4	4	6	3	4	17428.2026	-0.0016
4	3	2	4	2	2	5108.9019	-0.0040
4	3	1	4	2	3	5157.1563	0.0094
5	3	3	5	2	3	5064.2537	0.0035
5	3	2	5	2	4	5176.4172	0.0081
6	3	4	6	2	4	4989.1995	0.0085
6	3	3	6	2	5	5211.2954	0.0074
7	3	5	7	2	5	4876.2507	0.0040
7	3	4	7	2	6	5269.0365	0.0080
5	0	5	4	1	3	5839.3259	-0.0087
6	0	6	5	1	4	7043.9368	-0.0020
7	0	7	6	1	5	8174.2922	0.0071

Table S29: Measured rotational transition frequencies (ν_{obs}) for the **D2W2** with full deuterated water (DFM2-(D2O)2) and residual (ν_{obs}-ν_{calc}) for the fit of table S11 (frequencies in MHz).

J'	K_a'	K_c'	J"	K_a"	K_c"	ν_{obs}	ν_{obs}-ν_{calc}
7	0	7	6	0	6	9869.7600	-0.0103
6	0	6	5	0	5	8492.5247	0.0022
5	0	5	4	0	4	7103.7540	0.0056
8	0	8	7	0	7	11238.4386	-0.0175
9	0	9	8	0	8	12602.1267	0.0099
10	0	10	9	0	9	13963.7965	0.0459
11	0	11	10	0	10	15325.2765	-0.0081
6	1	6	5	1	5	8383.0932	0.0039
5	1	5	4	1	4	6992.5358	0.0046
7	1	7	6	1	6	9770.1913	-0.0056
8	1	8	7	1	7	11153.8822	-0.0222
9	1	9	8	1	8	12534.4374	0.0059
10	1	10	9	1	9	13912.1139	-0.0056
11	1	11	10	1	10	15287.3699	-0.0070
6	1	5	5	1	4	8769.0788	0.0062
5	1	4	4	1	3	7317.1008	0.0091
7	1	6	6	1	5	10213.7899	-0.0072
8	1	7	7	1	6	11649.2845	-0.0321
9	1	8	8	1	7	13073.5851	0.0010
10	1	9	9	1	8	14484.7548	-0.0133
11	1	10	10	1	9	15881.7413	-0.0136
5	2	4	4	2	3	7162.3128	0.0124
5	2	3	4	2	2	7228.4465	0.0079
6	2	5	5	2	4	8588.3282	0.0093
6	2	4	5	2	3	8699.4381	0.0132
7	2	6	6	2	5	10010.8723	-0.0100
7	2	5	6	2	4	10178.2079	-0.0184
8	2	7	7	2	6	11429.4777	-0.0170
8	2	6	7	2	5	11661.1573	-0.0003
9	2	8	8	2	7	12843.7421	0.0152
9	2	7	8	2	6	13143.8679	0.0007
10	2	9	9	2	8	14253.2411	-0.0012
10	2	8	9	2	7	14622.4336	0.0264
11	2	10	10	2	9	15657.8204	-0.0014
5	3	3	4	3	2	7180.7190	0.0138
6	3	4	5	3	3	8619.7802	0.0131
6	3	3	5	3	2	8626.0620	0.0159
7	3	5	6	3	4	10059.5316	-0.0085
7	3	4	6	3	3	10073.5173	0.0182
8	3	6	7	3	5	11499.5397	0.0194
8	3	5	7	3	4	11526.9325	0.0129
9	3	6	8	3	5	12987.8398	-0.0432
9	3	7	8	3	6	12939.0567	0.0193
10	3	8	9	3	7	14377.3141	0.0086

10	3	7	9	3	6	14457.7279	-0.0088
5	4	2	4	4	1	7177.7282	-0.0302
5	4	1	4	4	0	7177.7282	-0.0550
6	4	3	5	4	2	8615.6789	0.0375
6	4	2	5	4	1	8615.6789	-0.0740
7	4	4	6	4	3	10054.7360	-0.0038
7	4	3	6	4	2	10055.1201	0.0102
8	4	5	7	4	4	11495.1832	0.0055
8	4	4	7	4	3	11496.1933	0.0036
9	4	6	8	4	5	12937.0561	0.0430
9	4	5	8	4	4	12939.4670	0.0457
9	5	5	8	5	4	12927.7705	-0.0219
9	5	4	8	5	3	12927.8173	-0.0296
5	1	4	4	0	4	8616.1691	-0.0012
4	1	3	3	0	3	7001.2034	-0.0057
7	1	6	6	0	6	12002.7598	-0.0094
6	1	5	5	0	5	10281.5032	0.0088
3	2	1	2	1	1	7012.4923	-0.0293
3	2	2	2	1	2	7191.5912	0.0163
4	2	2	3	1	2	8381.8159	-0.0003
4	2	3	3	1	3	8723.0876	0.0112
5	2	3	4	1	3	9750.7020	0.0144
5	2	4	4	1	4	10286.6931	-0.0124
6	2	4	5	1	4	11133.0413	0.0206
6	2	5	5	1	5	11882.4908	-0.0023
7	2	5	6	1	5	12542.1557	-0.0188
7	2	5	6	1	5	12542.2024	0.0279
8	2	6	7	1	6	13989.5074	-0.0275
5	1	5	4	0	4	7638.4309	0.0184
7	1	7	6	0	6	10195.4052	-0.0226
8	1	8	7	0	7	11479.5553	-0.0066
6	0	6	5	1	5	7957.8461	-0.0123
7	0	7	6	1	6	9444.5216	-0.0178
8	0	8	7	1	7	10912.8096	0.0110

Table S30: Measured rotational transition frequencies (ν_{obs}) for the D13 isotopologue of **D2W2** and residual (ν_{obs}-ν_{calc}) for the fit of table S11 (frequencies in MHz).

J'	K_a'	K_c'	J"	K_a"	K_c"	ν_{obs}	ν_{obs}-ν_{calc}
5	0	5	4	0	4	7195.8986	-0.0014
5	1	5	4	1	4	7079.4521	-0.0018
5	1	4	4	1	3	7414.9704	-0.0032
5	2	4	4	2	3	7254.7321	0.0086
5	2	3	4	2	2	7321.1365	0.0071
6	0	6	5	0	5	8602.7202	-0.0020
6	1	6	5	1	5	8487.3233	0.0000
6	1	5	5	1	4	8886.5457	-0.0036
6	2	5	5	2	4	8699.2019	0.0007
6	2	4	5	2	3	8810.9974	0.0008
6	3	4	5	3	3	8730.8070	0.0049
7	0	7	6	0	6	9997.6075	0.0036
7	1	7	6	1	6	9891.6779	-0.0045
7	1	6	6	1	5	10350.8961	-0.0091
7	2	6	6	2	5	10140.1996	-0.0077
7	2	5	6	2	4	10309.0725	-0.0044
7	3	4	6	3	3	10202.7217	-0.0025
7	3	5	6	3	4	10189.1603	0.0058
8	0	8	7	0	7	11383.4011	0.0074
8	1	8	7	1	7	11292.5673	0.0054
8	1	7	7	1	6	11806.1217	0.0132
8	2	7	7	2	6	11577.2151	-0.0236
8	2	6	7	2	5	11811.8111	0.0075

Table S31: Measured rotational transition frequencies (ν_{obs}) for the D14 isotopologue of **D2W2** and residual (ν_{obs}-ν_{calc}) for the fit of table S11 (frequencies in MHz).

J'	K_a'	K_c'	J"	K_a"	K_c"	ν_{obs}	ν_{obs}-ν_{calc}
5	1	5	4	1	4	7087.1645	-0.0074
5	0	5	4	0	4	7202.4620	-0.0126
5	2	4	4	2	3	7256.7389	-0.0053
5	2	3	4	2	2	7317.9675	-0.0060
6	1	6	5	1	5	8497.1533	0.0022
6	0	6	5	0	5	8612.7585	-0.0046
6	1	5	5	1	4	8884.5792	-0.0044
6	2	4	5	2	3	8805.5544	-0.0112
6	3	3	5	3	2	8736.6167	-0.0054
6	3	4	5	3	3	8731.3160	0.0112
7	1	7	6	1	6	9903.8278	0.0021
7	0	7	6	0	6	10011.4979	0.0165
7	2	6	6	2	5	10144.3152	0.0093
7	2	5	6	2	4	10301.2860	-0.0034
7	1	6	6	1	5	10350.1358	0.0410
8	1	8	7	1	7	11307.1995	0.0060
8	0	8	7	0	7	11401.0326	-0.0051
8	2	6	7	2	5	11802.0770	-0.0079
8	1	7	7	1	6	11807.2921	-0.0121
9	1	9	8	1	8	12707.4329	0.0221
9	0	9	8	0	8	12784.6258	-0.0305

Table S32: Measured rotational transition frequencies (ν_{obs}) for the D13,14 isotopologue of **D2W2** and residual (ν_{obs}-ν_{calc}) for the fit of table S11 (frequencies in MHz).

J'	K_a'	K_c'	J"	K_a"	K_c"	ν_{obs}	ν_{obs}-ν_{calc}
7	1	7	6	1	6	9845.7336	-0.0153
6	1	6	5	1	5	8447.8559	0.0018
5	1	5	4	1	4	7046.4866	-0.0006
7	0	7	6	0	6	9950.1493	-0.0067
5	0	5	4	0	4	7161.3982	0.0113
8	0	8	7	0	7	11329.6692	-0.0008
9	0	9	8	0	8	12703.7247	0.0054
6	1	5	5	1	4	8842.1840	-0.0365
5	1	4	4	1	3	7377.9051	0.0185
8	1	8	7	1	7	11240.2319	0.0308
8	1	7	7	1	6	11747.6086	0.0126
9	1	9	8	1	8	12631.3889	-0.0198
5	2	3	4	2	2	7285.3870	0.0113
5	2	4	4	2	3	7219.6284	-0.0100

Table S33: Measured rotational transition frequencies (ν_{obs}) for the D13,14,16 isotopologue of **D2W2** and residual (ν_{obs}-ν_{calc}) for the fit of table S11 (frequencies in MHz).

J'	K_a'	K_c'	J"	K_a"	K_c"	ν_{obs}	ν_{obs}-ν_{calc}
5	0	5	4	0	4	7116.0757	0.0014
5	1	5	4	1	4	7002.7034	0.0034
5	1	4	4	1	3	7333.9267	0.0040
5	2	3	4	2	2	7243.6306	-0.0081
5	2	4	4	2	3	7175.9756	-0.0120
6	0	6	5	0	5	8506.6051	0.0082
6	1	6	5	1	5	8395.1073	-0.0037
6	2	5	5	2	4	8604.5845	-0.0061
6	2	4	5	2	3	8718.2153	0.0032
6	3	4	5	3	3	8636.7643	-0.0082
6	3	3	5	3	2	8643.2172	0.0073
7	0	7	6	0	6	9885.3580	-0.0031

7	1	7	6	1	6	9783.9989	0.0030
7	1	6	6	1	5	10236.6293	0.0034
7	2	5	6	2	4	10200.7404	0.0004
8	1	8	7	1	7	11169.3998	-0.0082
8	0	8	7	0	7	11255.4119	0.0021
8	1	7	7	1	6	11674.8373	0.0019
9	1	8	8	1	7	13101.5170	-0.0110
8	2	7	7	2	6	11450.7023	0.0198

Table S34: Measured rotational transition frequencies (ν_{obs}) for the parent species of **DW3** and residual (ν_{obs}-ν_{calc}) for the fit of table S12 (frequencies in MHz).

J'	K_a'	K_c'	J"	K_a"	K_c"	ν_{obs}	ν_{obs}-ν_{calc}
1	0	1	0	0	0	2287.5848	0.0122
2	1	2	1	1	1	4498.2013	0.0038
2	0	2	1	0	1	4572.3729	0.0015
2	1	1	1	1	0	4651.9760	0.0018
3	0	3	2	0	2	6851.6490	0.0029
3	1	3	2	1	2	6745.5529	0.0043
3	2	2	2	2	1	6862.3818	-0.0267
3	2	1	2	2	0	6873.3899	0.0028
3	1	2	2	1	1	6976.1507	0.0026
4	1	4	3	1	3	8990.8941	0.0065
4	0	4	3	0	3	9122.7672	0.0051
4	2	3	3	2	2	9147.6260	0.0036
4	3	2	3	3	1	9154.7439	0.0065
4	3	1	3	3	0	9155.1138	0.0071
4	2	2	3	2	1	9174.9197	0.0030
4	1	3	3	1	2	9298.0607	0.0018
5	1	5	4	1	4	11233.6909	0.0091
5	0	5	4	0	4	11383.4273	0.0075
5	2	4	4	2	3	11430.9071	0.0019
5	4	2	4	4	1	11442.0983	0.0082
5	4	1	4	4	0	11442.0972	-0.0020
5	3	3	4	3	2	11445.4091	-0.0008
5	3	2	4	3	1	11446.6976	-0.0026
5	2	3	4	2	2	11484.8748	0.0011
5	1	4	4	1	3	11616.8025	-0.0026
6	1	6	5	1	5	13473.5214	0.0116
6	0	6	5	0	5	13632.0140	0.0061
6	2	5	5	2	4	13711.7884	0.0077
6	4	3	5	4	2	13732.2620	0.0181
6	4	2	5	4	1	13732.2620	-0.0230
6	3	4	5	3	3	13737.0856	-0.0032
6	3	3	5	3	2	13740.5132	-0.0056
6	2	4	5	2	3	13804.3549	0.0024
6	1	5	5	1	4	13931.3531	-0.0053
7	1	7	6	1	6	15710.0765	-0.0011
7	0	7	6	0	6	15868.0154	0.0106
7	2	6	6	2	5	15989.7779	-0.0037
7	4	4	6	4	3	16023.3106	-0.0137
7	4	3	6	4	2	16023.4505	-0.0109
7	3	5	6	3	4	16029.6730	-0.0023
7	3	4	6	3	3	16037.3531	-0.0002
7	2	5	6	2	4	16133.3342	-0.0105
7	1	6	6	1	5	16240.5225	-0.0109
8	1	8	7	1	7	17943.2246	-0.0027
6	5	2	5	5	1	13728.8447	-0.0009
6	5	1	5	5	0	13728.8447	-0.0011
7	5	3	6	5	2	16018.3598	0.0041
7	5	2	6	5	1	16018.3598	0.0031
1	1	1	0	0	0	3861.2336	0.0030
6	2	4	6	1	5	4238.8550	0.0066
5	2	3	5	1	4	4365.8589	0.0044
4	2	2	4	1	3	4497.7907	0.0046
3	2	1	3	1	2	4620.9349	0.0066
2	2	0	2	1	1	4723.6877	-0.0014
3	2	2	3	1	3	5068.4770	0.0125
4	2	3	4	1	4	5225.2110	0.0116
3	0	3	2	1	2	5352.1617	-0.0002
5	2	4	5	1	5	5422.4237	0.0009
6	2	5	6	1	6	5660.7008	0.0070
5	1	4	4	2	3	7160.0422	-0.0001
2	1	2	1	0	1	6071.8562	0.0006

4	0	4	3	1	3	7729.3782	0.0027
3	1	3	2	0	2	8245.0353	0.0024
2	2	1	1	1	0	9372.9139	0.0010
2	2	0	1	1	1	9452.5539	0.0014
5	0	5	4	1	4	10121.9078	0.0001
4	1	4	3	0	3	10384.2737	-0.0005
3	2	2	2	1	1	11583.3476	0.0002
5	1	5	4	0	4	12495.2003	0.0065
6	0	6	5	1	5	12520.2341	0.0001
4	2	3	3	1	2	13754.8208	-0.0009
4	2	2	3	1	3	14257.1078	-0.0022
6	1	6	5	0	5	14585.2866	0.0028
7	0	7	6	1	6	14914.7296	0.0006
3	3	1	2	2	0	14921.7585	-0.0131
3	3	0	2	2	1	14924.5789	-0.0048
5	2	3	4	1	4	16751.0930	-0.0031
4	3	2	3	2	1	17203.1070	-0.0149
4	3	1	3	2	2	17217.2585	-0.0232
8	0	8	7	1	7	17296.8757	-0.0013
7	1	7	6	0	6	16663.3546	0.0012
5	2	4	4	1	3	15887.6739	0.0057
3	3	0	2	2	1	14924.5789	-0.0048
3	3	1	2	2	0	14921.7585	-0.0131
7	3	4	7	2	5	7830.6505	0.0126
6	3	3	6	2	4	7926.6344	0.0050
5	3	2	5	2	3	7990.4673	0.0045
4	3	1	4	2	2	8028.6324	-0.0037
3	3	0	3	2	1	8048.4507	0.0044
3	3	1	3	2	2	8062.1166	0.0031
4	3	2	4	2	3	8069.2318	0.0033
5	3	3	5	2	4	8083.7388	0.0055
6	3	4	6	2	5	8109.0455	0.0039
7	3	5	7	2	6	8148.9364	0.0011
6	1	5	5	2	4	9660.5073	0.0117
7	1	6	6	2	5	12189.2553	0.0069
8	1	7	7	2	6	14742.4463	0.0099
5	4	2	5	3	3	11276.3649	-0.0324
5	4	1	5	3	2	11274.7065	0.0199
6	4	3	6	3	4	11271.5609	0.0085
6	4	2	6	3	3	11266.4667	0.0140
7	4	4	7	3	5	11265.2084	0.0071
7	4	3	7	3	4	11252.5538	-0.0069

11] **COMPARISON** BETWEEN DIFFERENT METHODS OF CALCULATIONS AND THE EXPERIMENT

Table S35: Rotational constants obtained by MP2/6-311++G**, B3LYP-D3BJ/6-311++G** and B3LYP-D3BJ/def2tzvp. The comparison with experiment shows a general better performance of MP2 geometrical arrangements, even if in the majority of cases the three set of data are of comparable accuracy. However, for the DW2 complex, the B3LYP-D3BJ/6-311++G** fails in predicting the correct geometry, as deduced from the large differences between the theoretical and experimental rotational constants (highlighted in red). We can assert that in this case the B3LYP-D3BJ/6-311++G** is unable to find the correct minimum.

D2W	ν_0	ν_1	MP2/6-311++G**	B3LYP-D3BJ/6-311++G**	B3LYP-D3BJ/def2tzvp
A/MHz	2248.046(7)	2248.189(7)	2304.9	2213.1	2329.9
B/MHz	1096.505(1)	1096.513(1)	1103.4	1125.2	1100.5
C/MHz	860.5630(6)	860.5101(6)	873.4	871.1	919.2
		Δ*A*/MHz	-57	35	-82
		Δ*B*/MHz	-7	-29	-4
		Δ*C*/MHz	-13	-11	-59
BE kJ/mol			**-28.0**	**-32.4**	**-29.2**
DW2	ν_0	ν_1	MP2/6-311++G**	B3LYP-D3BJ/6-311++G**	B3LYP-D3BJ/def2tzvp
A/MHz	5249.79(8)	5249.99(9)	5560.0	4276.5	5296.2
B/MHz	1729.538(3)	1729.659(3)	1736.1	2004.6	1767.9
C/MHz	1316.198(2)	1316.167(3)	1339.4	1602.3	1345.1
		Δ*A*/MHz	-310	973	-46
		Δ*B*/MHz	-7	-275	-38
		Δ*C*/MHz	-23	-286	-29
BE kJ/mol			**-41.7**	**-43.1**	**-41.9**
D2W2	ν_0		MP2/6-311++G**	B3LYP-D3BJ/6-311++G**	B3LYP-D3BJ/def2tzvp
A/MHz	1759.4166(4)		1744.2	1652.4	1652.6
B/MHz	763.3093(1)		737.2	762.3	752.5
C/MHz	696.9655(1)		699.5	692.1	674.5
		Δ*A*/MHz	15	107	107
		Δ*B*/MHz	26	1	11
		Δ*C*/MHz	-3	5	22
BE kJ/mol			**-53.0**	**-60.6**	**-58.6**
DW3	ν_0		MP2/6-311++G**	B3LYP-D3BJ/6-311++G**	B3LYP-D3BJ/def2tzvp
A/MHz	2755.9026		2803.6	2858.5	2853.9
B/MHz	1182.23300		1212.3	1236.5	1225.8
C/MHz	1105.34360		1139.1	1149.1	1139.1
		Δ*A*/MHz	-48	-103	-98
		Δ*B*/MHz	-30	-54	-44
		Δ*C*/MHz	-34	-44	-34
BE kJ/mol			**-73.5**	**-77.3**	**-78.2**

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