Electronic Supporting Information

Conformational Adaptation and Large Amplitude Motions of 1-Phenyl-2,2,2-Trifluoroethanol with Two Water Molecules: A Rotational Spectroscopic and Ab Initio Investigation

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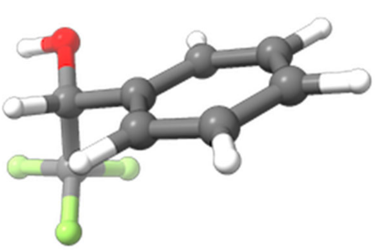
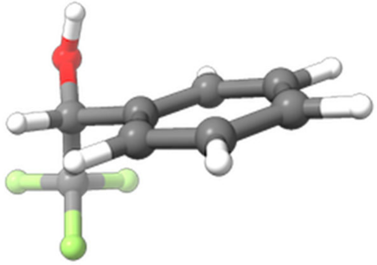
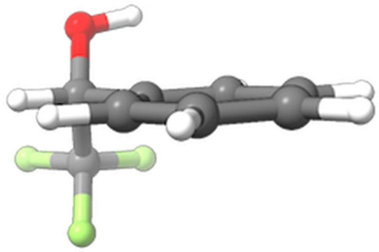
Table S1. Raw (ΔE_e), ZPE-corrected ($\Delta E_{0,a}$), and ZPE+BSSE-corrected ($\Delta E_{0,b}$) relative energies (in kJ mol^{-1}), rotational constants (in MHz), dipole moment components (in Debye), and the $C_{benzene}COH$ torsion, τ (in degrees, 0 to 360), for the PhTFE subunit in the computationally identified PhTFE···2H_2O conformers calculated at the B3LYP-D3BJ/def2-TZVPPD level of theory.

	τ(CCOH)	Energies (kJ mol^{-1})			Dip. Mom. (D)			Rot. Const. (MHz)		
Structure[a]	deg.	ΔE_e	$\Delta E_{0,a}$	$\Delta E_{0,b}$	μ_a	μ_b	μ_c	*A*	*B*	*C*
II-2W-**1**	167	0.0	0.0	0.0	-5.1	-0.3	-1.3	853	469	364
II-2W-**2**	170	0.8	0.4	0.4	-5.2	-0.4	-1.2	857	465	366
II-2W-**3**	164	0.8	0.4	0.4	-4.9	0.0	-0.2	865	468	369
III-2W-**4**	277	2.6	4.5	4.4	1.3	0.9	0.3	940	444	356
II-2W-**5**	195	2.7	4.4	4.4	-2.4	0.4	0.2	699	545	383
I-2W-**6**	94	3.1	4.0	3.9	1.5	2.5	1.2	676	518	356
II-2W-**7**	153	3.4	4.4	4.2	0.2	2.0	1.0	851	418	335
III-2W-**8**	298	3.6	5.9	5.9	-2.7	0.1	-0.1	721	536	388
I-2W-**9**	76	4.2	4.8	4.6	0.1	2.9	-0.7	717	472	338
I-2W-**10**	81	4.2	5.4	5.4	0.5	0.8	0.8	1036	388	346
I-2W-**11**	69	4.5	5.4	5.2	0.7	2.5	1.2	745	461	339
I-2W-**12**	73	5.2	6.3	6.2	0.7	-1.5	-0.3	1020	398	346
III-2W-**13**	293	5.3	6.7	6.7	0.8	0.7	1.0	926	429	348
II-2W-**14**	176	5.4	6.1	5.9	0.5	2.2	1.2	751	453	335
I-2W-**15**	63	5.5	6.5	6.3	1.1	1.1	0.6	906	413	338
a**III**-2W-**16**	288	5.5	7.0	7.1	-2.5	-0.8	1.0	871	516	439
III-2W-**17**	292	5.6	7.1	7.0	1.0	-1.2	-0.9	975	431	350
III-2W-**18**	298	6.0	7.4	7.3	0.1	2.1	1.2	635	549	368
II-2W-**19**	201	6.6	6.8	6.7	1.8	1.4	0.3	682	546	369
a**III**-2W-**20**	283	7.1	7.6	7.6	-4.6	-1.1	0.7	904	464	397
a**III**-2W-**21**	263	7.4	9.2	9.1	-3.0	-0.1	-1.3	678	518	380
a**III**-2W-**22**	292	8.4	8.6	8.7	-3.7	-0.3	0.3	869	513	437
III-2W-**23**	305	8.9	9.6	9.5	1.8	1.9	0.5	642	552	364
I-2W-**24**	94	9.0	8.3	8.1	-2.0	0.6	2.4	1057	357	330
I-2W-**25**	89	9.1	8.2	8.0	-0.8	0.1	0.7	1164	346	315
I-2W-**26**	62	10.0	10.0	10.0	-1.7	0.4	0.3	713	519	400
III-2W-**27**	290	10.4	10.1	10.0	-0.3	1.6	-1.7	864	446	356
a**III**-2W-**28**	284	14.2	14.3	14.2	-2.7	0.4	1.8	637	531	374
a**III**-2W-**29**	268	14.4	13.8	13.7	0.6	0.8	-1.2	658	507	362
a**III**-2W-**30**	273	17.1	16.2	16.2	1.9	-1.8	-1.5	728	499	411
I-2W-**31**	54	19.3	18.0	17.8	0.5	-0.9	-2.8	710	476	357
II-2W-**32**	178	19.4	16.8	16.8	-5.2	1.7	1.6	734	510	400

I-2W-**33**	79	21.5	18.9	18.7	-2.5	1.6	-1.6	928	397	359
II-2W-**34**	196	21.7	19.9	19.9	-5.6	-1.2	-3.5	729	530	390
I-2W-**35**	58	22.5	20.7	20.7	-1.7	-2.5	1.5	877	452	368
a**III**-2W-**36**	282	22.9	20.6	20.5	0.4	-1.2	3.1	697	480	412
I-2W-**37**	69	23.0	21.5	21.3	1.2	-1.7	-2.0	643	552	344
I-2W-**38**	57	23.2	21.0	21.0	-1.7	-2.3	-0.4	904	445	366

PhTFE **I**	PhTFE **II**	PhTFE **III**
		

[a] Structures containing an "a" prior to the Roman numerals describing the configuration of the PhTFE subunit are highly distorted from its free, isolated form. In the isolated PhTFE monomers, τ has values of 57, 169, and 277 degrees for PhTFE **I**, **II**, and **III**, respectively. The optimized PhTFE monomer structures are provided at the bottom.

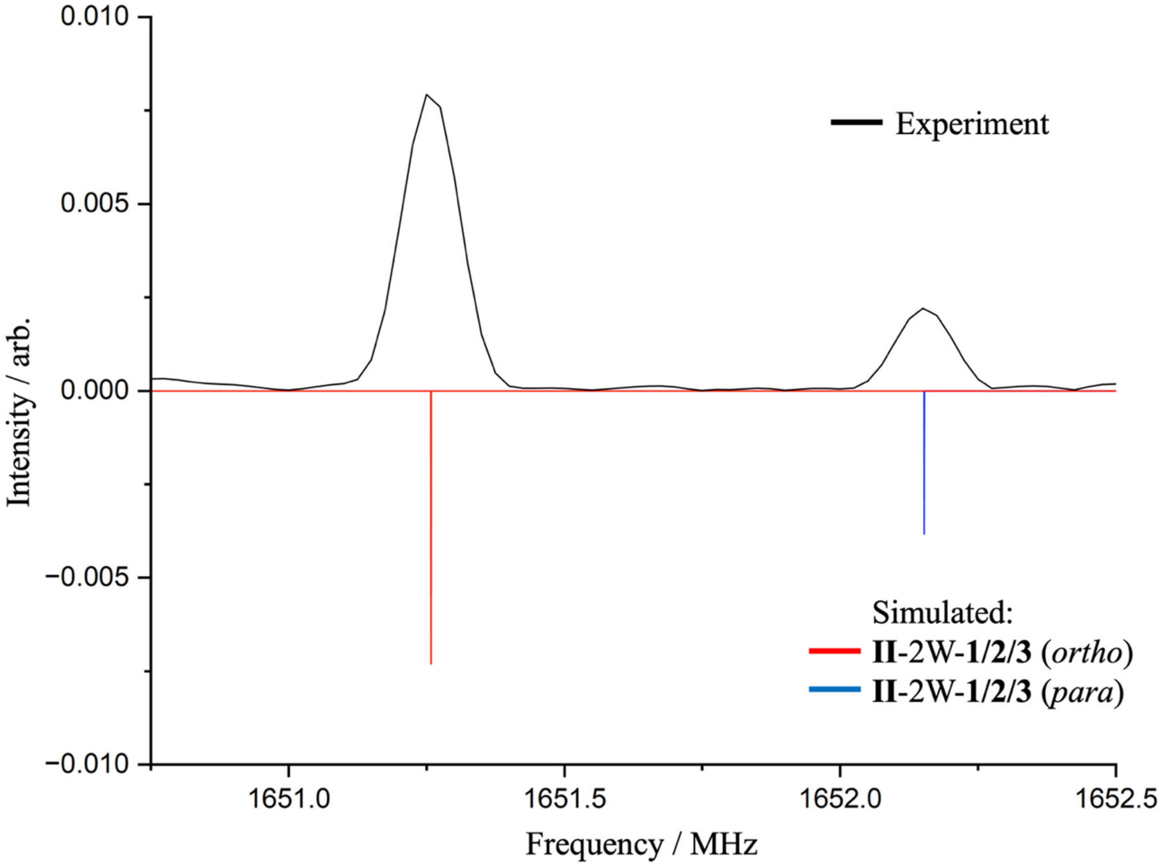


Figure S1. A zoom-in section of the rotational spectrum showing the *ortho*-*para* splitting in the $2_{0,2} \rightarrow 1_{0,1}$ *a*-type transition of **II**-2W-**1**/**2**/**3**.

Table S2.1. **II**-2W-**1**/**2**/**3** (*ortho)* assigned transitions, along with their frequencies and deviation from the calculated value ($\Delta\nu = \nu - \nu_{calc}$).

J	K_a	K_c	J'	K_a'	K_c'	ν/ MHz	$\Delta\nu$/ MHz
2	1	2	1	1	1	1567.9128	-0.0007
2	0	2	1	0	1	1651.2583	0.0003
2	1	1	1	1	0	1769.3029	0.0001
2	1	1	1	0	1	2253.6248	0.0031
3	1	3	2	1	2	2341.8214	0.0014
3	0	3	2	0	2	2436.6675	-0.0014
3	2	1	2	2	0	2569.1513	-0.0007
3	1	2	2	1	1	2642.0004	-0.0002
6	3	4	6	1	5	2885.6753	0.0010
2	2	0	1	1	0	2937.5185	-0.0009
5	3	3	5	1	4	2947.9485	-0.0020
5	4	1	5	3	3	3009.1101	-0.0019
8	1	7	8	1	8	3011.6935	0.0014
2	2	1	1	1	1	3020.8685	0.0040
8	3	6	8	1	7	3024.7836	-0.0011
4	1	4	3	1	3	3106.0976	0.0016
4	0	4	3	0	3	3187.8774	-0.0023
8	2	7	8	0	8	3189.1261	-0.0025
9	3	7	9	1	8	3240.8236	0.0033
4	2	3	3	2	2	3323.6177	0.0004
4	3	2	3	3	1	3366.9407	0.0009
4	3	1	3	3	0	3378.1242	0.0020
2	2	0	1	0	1	3421.8386	0.0003
4	2	2	3	2	1	3472.7754	0.0018
4	1	3	3	1	2	3497.6887	0.0004
10	3	8	10	1	9	3536.5616	-0.0016
11	2	9	11	2	10	3559.4368	0.0022
9	2	8	9	0	9	3600.2997	-0.0018
3	2	1	2	1	1	3737.3715	0.0029
5	1	5	4	1	4	3860.8678	-0.0008
3	2	2	2	1	2	3955.8627	0.0003
5	2	4	4	2	3	4133.0508	-0.0009
5	4	1	4	4	0	4211.3334	-0.0001
5	3	3	4	3	2	4213.9367	0.0014
5	3	2	4	3	1	4251.3608	-0.0017
5	1	4	4	1	3	4326.8918	-0.0001
3	2	1	2	0	2	4339.7351	0.0028
5	2	3	4	2	2	4385.7759	0.0000

4	2	2	3	1	2	4568.1428	0.0012
6	1	6	5	1	5	4607.7404	-0.0011
6	0	6	5	0	5	4641.0282	-0.0013
3	3	0	2	2	0	4667.3409	-0.0010
3	3	1	2	2	1	4682.7903	0.0007
6	2	5	5	2	4	4929.3049	0.0005
4	2	3	3	1	3	4937.6593	-0.0003
6	5	2	5	5	1	5049.7363	-0.0007
6	5	1	5	5	0	5049.8753	-0.0015
6	3	4	5	3	3	5057.8621	-0.0001
6	4	3	5	4	2	5062.9628	0.0013
6	4	2	5	4	1	5068.9466	0.0005
6	1	5	5	1	4	5120.1377	-0.0007
6	3	3	5	3	2	5149.4763	-0.0012
6	2	4	5	2	3	5288.0841	0.0001
7	1	7	6	1	6	5348.9426	-0.0015
7	0	7	6	0	6	5366.5674	0.0010
4	2	2	3	0	3	5375.8365	-0.0005
5	1	4	4	0	4	5444.3988	0.0029
5	2	3	4	1	3	5456.2247	-0.0044
4	3	1	3	2	1	5476.3111	-0.0009
4	3	2	3	2	2	5546.8203	0.0023
7	2	6	6	2	5	5711.5409	-0.0017
7	1	6	6	1	5	5874.6142	-0.0026
7	6	1	6	6	0	5889.3707	-0.0065
7	6	2	6	6	1	5889.3707	0.0064
7	5	3	6	5	2	5902.2913	0.0000
7	5	2	6	5	1	5903.0509	0.0029
7	4	4	6	4	3	5919.3938	-0.0006
7	4	3	6	4	2	5938.5449	-0.0011
5	2	4	4	1	4	5964.6169	0.0016
7	3	4	6	3	3	6072.8094	0.0013
8	1	8	7	1	7	6086.5568	0.0014
8	0	8	7	0	7	6095.2674	-0.0004
7	2	5	6	2	4	6165.8938	0.0018
5	3	2	4	2	2	6254.9013	0.0004
4	4	0	3	3	0	6376.7502	-0.0013
4	4	1	3	3	1	6378.4844	0.0032
6	2	4	5	1	4	6417.4203	-0.0010
5	3	3	4	2	3	6437.1354	-0.0006
8	2	7	7	2	6	6480.2981	-0.0029
5	2	3	4	0	4	6573.7279	-0.0052

8	1	7	7	1	6	6600.2973	-0.0001
8	3	6	7	3	5	6719.6224	-0.0011
8	7	2	7	7	1	6729.1362	0.0012
8	7	1	7	7	0	6729.1362	0.0001
8	6	3	7	6	2	6740.7725	0.0008
8	6	2	7	6	1	6740.8549	0.0003
8	5	4	7	5	3	6759.4685	-0.0003
8	5	3	7	5	2	6762.4198	0.0004
8	4	5	7	4	4	6776.9517	-0.0036
9	1	9	8	1	8	6822.1165	0.0006
9	0	9	8	0	8	6826.2347	0.0045

Table S2.2. II-2W-**1**/**2**/**3** (*para)* assigned transitions, along with their frequencies and deviation from the calculated value ($\Delta\nu = \nu - \nu_{calc}$).

J	***K*$_a$**	***K*$_c$**	***J'***	***K*$_a$'**	***K*$_c$'**	ν/ MHz	Δν/ MHz
2	0	2	1	0	1	1652.1522	-0.0010
2	1	1	1	1	0	1772.6766	-0.0026
3	1	3	2	1	2	2341.0777	0.0004
3	2	2	2	2	1	2505.2595	0.0003
3	2	1	2	2	0	2573.9247	-0.0100
2	2	0	1	1	0	2935.3984	-0.0007
2	2	1	1	1	1	3019.8842	-0.0010
8	3	6	8	1	7	3031.2812	0.0026
4	1	4	3	1	3	3104.5508	0.0026
4	0	4	3	0	3	3186.0363	-0.0064
4	2	3	3	2	2	3326.2203	0.0024
4	3	2	3	3	1	3371.1251	-0.0012
4	3	1	3	3	0	3382.9763	0.0021
2	2	0	1	0	1	3419.4758	0.0021
4	2	2	3	2	1	3480.3259	-0.0006
4	1	3	3	1	2	3502.7156	-0.0018
9	2	8	9	0	9	3633.4785	-0.0052
3	2	1	2	1	1	3736.6539	-0.0007
5	1	5	4	1	4	3858.2860	0.0072
5	0	5	4	0	4	3913.9190	-0.0001
3	2	2	2	1	2	3957.4753	-0.0014
5	2	4	4	2	3	4135.4834	0.0010
5	4	2	4	4	1	4215.3691	0.0043
5	4	1	4	4	0	4216.8384	0.0000
5	3	3	4	3	2	4219.1725	-0.0044
5	3	2	4	3	1	4258.7519	-0.0004
5	1	4	4	1	3	4331.2032	-0.0005

3	2	1	2	0	2	4341.2565	0.0013
5	2	3	4	2	2	4395.5035	-0.0010
4	2	2	3	1	2	4570.4158	0.0102
6	1	6	5	1	5	4603.9883	0.0013
3	3	0	2	2	0	4663.7566	0.0006
3	3	1	2	2	1	4679.7575	-0.0013
6	2	5	5	2	4	4931.1112	0.0033
6	5	2	5	5	1	5056.1496	0.0000
6	5	1	5	5	0	5056.3053	0.0012
6	3	4	5	3	3	5063.8531	-0.0011
6	4	3	5	4	2	5069.7829	-0.0030
6	4	2	5	4	1	5076.2572	0.0027
6	1	5	5	1	4	5122.3361	-0.0029
6	3	3	5	3	2	5160.3606	0.0019
6	2	4	5	2	3	5298.8047	-0.0014
7	1	7	6	1	6	5344.0006	0.0002
7	0	7	6	0	6	5360.9045	-0.0017
4	2	2	3	0	3	5385.0003	0.0001
5	1	4	4	0	4	5462.4756	0.0026
5	2	3	4	1	3	5463.1897	-0.0029
4	3	1	3	2	1	5472.7966	0.0012
4	3	2	3	2	2	5545.6251	-0.0008
7	2	6	6	2	5	5712.3004	-0.0018
7	1	6	6	1	5	5873.8458	-0.0032
7	6	2	6	6	1	5896.7696	-0.0014
7	6	1	6	6	0	5896.7845	-0.0011
7	3	5	6	3	4	5900.6682	0.0013
7	5	3	6	5	2	5910.1861	0.0002
7	5	2	6	5	1	5911.0215	0.0002
7	4	4	6	4	3	5927.6513	-0.0001
7	4	3	6	4	2	5948.3117	-0.0014
5	2	4	4	1	4	5973.5493	-0.0021
8	1	8	7	1	7	6080.4496	-0.0020
7	3	4	6	3	3	6087.4881	0.0033
8	0	8	7	0	7	6088.7125	0.0005
7	2	5	6	2	4	6176.2726	0.0007
4	4	0	3	3	0	6371.8766	-0.0010
4	4	1	3	3	1	6373.7096	0.0016

8	2	7	7	2	6	6479.7134	-0.0026
8	1	7	7	1	6	6596.9016	-0.0040
8	3	6	7	3	5	6725.5817	-0.0041
8	7	1	7	7	0	6737.5374	-0.0020
8	7	2	7	7	1	6737.5374	-0.0007
8	6	3	7	6	2	6749.6275	-0.0015
8	6	2	7	6	1	6749.7263	0.0039
8	5	4	7	5	3	6768.9907	0.0009
8	5	3	7	5	2	6772.2491	0.0058
8	4	5	7	4	4	6786.4619	0.0011
9	1	9	8	1	8	6814.8964	0.0010
9	0	9	8	0	8	6818.7509	-0.0011
8	4	4	7	4	3	6839.4484	0.0084

Table S2.3. II-2W-**1/2/3** ($^{18}O^{18}O$) assigned transitions, along with their frequencies and deviation from the calculated value ($\Delta\nu = \nu - \nu_{calc}$).

J	K_a	K_c	J'	K_a'	K_c'	ν/ MHz	$\Delta\nu$/ MHz
3	1	3	2	1	2	2267.4727	0.0042
3	0	3	2	0	2	2360.5253	-0.0069
4	1	4	3	1	3	3006.0094	0.0028
4	0	4	3	0	3	3083.8763	0.0001
4	2	3	3	2	2	3226.9495	-0.0024
4	3	1	3	3	0	3285.7988	-0.0001
4	2	2	3	2	1	3384.4008	0.0021
4	1	3	3	1	2	3401.2091	0.0020
5	1	5	4	1	4	3734.7549	0.0120
5	0	5	4	0	4	3786.6707	0.0018
5	2	4	4	2	3	4010.7091	-0.0003
5	4	2	4	4	1	4093.1146	-0.0014
5	4	1	4	4	0	4094.7503	-0.0042
5	3	3	4	3	2	4096.4659	-0.0023
5	3	2	4	3	1	4138.6509	0.0026
5	1	4	4	1	3	4202.3761	-0.0063
5	2	3	4	2	2	4274.2999	-0.0074
6	1	6	5	1	5	4455.5532	0.0084
6	0	6	5	0	5	4485.0033	-0.0010
6	2	5	5	2	4	4780.4998	0.0028
6	3	4	5	3	3	4915.9856	0.0016
6	4	3	5	4	2	4923.3026	-0.0049
6	4	2	5	4	1	4930.4865	0.0017

6	1	5	5	1	4	4965.0535	-0.0054
6	3	3	5	3	2	5018.0857	0.0022
5	2	3	4	1	3	5298.0074	0.0081
7	2	6	6	2	5	5535.6366	-0.0022
7	1	6	6	1	5	5688.1683	-0.0084
7	6	2	6	6	1	5725.5505	0.0164
7	6	1	6	6	0	5725.5505	-0.0011
7	3	5	6	3	4	5727.0292	-0.0050
7	4	4	6	4	3	5756.7996	0.0034
7	4	3	6	4	2	5779.6373	-0.0010
8	1	8	7	1	7	5882.7493	0.0022
8	0	8	7	0	7	5889.9484	0.0028
7	3	4	6	3	3	5922.4663	0.0019
7	2	5	6	2	4	5999.5245	-0.0046
8	2	7	7	2	6	6276.9811	-0.0070
8	3	6	7	3	5	6525.5664	0.0013
8	3	5	7	3	4	6835.5293	0.0089

Table S2.4. II-2W-**1/2/3** ($^{16}O^{18}O$) assigned transitions, along with their frequencies and deviation from the calculated value ($\Delta\nu = \nu - \nu_{calc}$).

J	K_a	K_c	J'	K_a'	K_c'	ν/ MHz	Δν/ MHz
3	1	3	2	1	2	2295.5148	-0.0015
3	0	3	2	0	2	2389.3885	0.0074
4	2	2	3	2	1	3397.1752	-0.0035
4	1	3	3	1	2	3426.3358	-0.0039
5	0	5	4	0	4	3844.1423	-0.0070
5	2	4	4	2	3	4050.0283	0.0003
5	3	2	4	3	1	4160.2964	0.0004
5	1	4	4	1	3	4240.9026	-0.0018
5	2	3	4	2	2	4290.7671	0.0027
6	1	6	5	1	5	4518.8458	-0.0024
6	0	6	5	0	5	4553.9203	0.0010
6	2	5	5	2	4	4831.4986	0.0101
6	3	4	5	3	3	4953.1989	0.0013
6	4	3	5	4	2	4956.9733	0.0046
6	4	2	5	4	1	4962.1982	0.0044
6	1	5	5	1	4	5021.8185	0.0027
6	2	4	5	2	3	5175.6113	-0.0074
7	1	7	6	1	6	5246.1568	-0.0028
7	0	7	6	0	6	5265.1335	0.0003
7	2	6	6	2	5	5599.6244	0.0020
7	1	6	6	1	5	5765.4665	-0.0030

7	3	5	6	3	4	5773.4536	-0.0015
7	5	3	6	5	2	5778.7476	-0.0001
7	4	3	6	4	2	5812.0034	0.0000
7	3	4	6	3	3	5938.0632	-0.0026
8	1	8	7	1	7	5969.8254	-0.0016
7	2	5	6	2	4	6038.1789	0.0011
8	2	7	7	2	6	6354.7804	0.0004
9	0	9	8	0	8	6695.9801	0.0012

Table S2.5. II-2W-**1/2/3** (^{18}O^{16}O) assigned transitions, along with their frequencies and deviation from the calculated value ($\Delta\nu = \nu - \nu_{calc}$).

J	K_a	K_c	J'	K_a'	K_c'	ν/ MHz	Δν/ MHz
3	1	3	2	1	2	2312.2988	0.0047
4	1	4	3	1	3	3064.6856	-0.0017
4	0	4	3	0	3	3141.4328	-0.0044
4	2	3	3	2	2	3293.0001	-0.0008
4	2	2	3	2	1	3459.9634	-0.0048
4	1	3	3	1	2	3471.1386	-0.0027
5	1	5	4	1	4	3806.8541	-0.0027
5	0	5	4	0	4	3856.7249	0.0042
5	3	2	4	3	1	4229.7132	0.0009
5	1	4	4	1	3	4285.7454	-0.0034
5	2	3	4	2	2	4368.8046	-0.0026
6	1	6	5	1	5	4540.9058	-0.0015
6	2	5	5	2	4	4875.4025	-0.0030
6	4	3	5	4	2	5028.2255	0.0051
6	1	5	5	1	4	5059.2058	0.0039
6	3	3	5	3	2	5131.3344	0.0078
6	2	4	5	2	3	5261.5697	0.0012
7	1	7	6	1	6	5269.4414	0.0000
7	0	7	6	0	6	5283.1823	0.0030
7	2	6	6	2	5	5643.7718	0.0038
7	1	6	6	1	5	5791.9444	0.0007
7	3	5	6	3	4	5845.5745	0.0066
7	5	3	6	5	2	5861.6896	-0.0043
7	5	2	6	5	1	5862.8507	-0.0076
7	4	4	6	4	3	5879.6861	0.0039
7	4	3	6	4	2	5906.0506	-0.0016
8	0	8	7	0	7	6001.1015	0.0002
7	3	4	6	3	3	6057.9087	-0.0015
7	2	5	6	2	4	6124.2939	0.0013
8	2	7	7	2	6	6397.8375	-0.0056

8	1	7	7	1	6	6499.4344	-0.0006

Table S2.6. **II**-2W-**1**/**2**/**3** (OD-HOH-HOH) assigned transitions, along with their frequencies and deviation from the calculated value ($\Delta\nu = \nu - \nu_{calc}$).

J	K_a	K_c	J'	K_a'	K_c'	ν/ MHz	Δν/ MHz
3	1	3	2	1	2	2335.0667	-0.0020
3	1	2	2	1	1	2638.4574	-0.0025
4	1	4	3	1	3	3096.5874	0.0004
4	0	4	3	0	3	3177.0909	-0.0042
4	2	3	3	2	2	3316.8014	-0.0004
4	3	2	3	3	1	3361.6075	0.0039
4	1	3	3	1	2	3491.9192	-0.0019
5	1	5	4	1	4	3848.4140	-0.0015
5	0	5	4	0	4	3903.2080	-0.0021
5	2	4	4	2	3	4123.7550	-0.0027
5	4	1	4	4	0	4204.9792	0.0049
5	3	3	4	3	2	4207.2247	0.0088
5	3	2	4	3	1	4246.8891	0.0004
5	1	4	4	1	3	4317.7420	-0.0019
5	2	3	4	2	2	4382.6760	0.0032
6	1	6	5	1	5	4592.2799	-0.0010
6	0	6	5	0	5	4624.0190	-0.0005
6	5	2	5	5	1	5041.9112	-0.0026
6	5	1	5	5	0	5042.0709	0.0006
6	3	4	5	3	3	5049.4138	-0.0024
6	4	2	5	4	1	5062.0158	0.0006
6	1	5	5	1	4	5106.2850	-0.0041
6	3	3	5	3	2	5146.0640	-0.0019
7	1	7	6	1	6	5330.5130	0.0039
7	0	7	6	0	6	5347.0570	0.0028
7	2	6	6	2	5	5696.0980	0.0007
7	1	6	6	1	5	5855.4480	-0.0005
7	3	5	6	3	4	5883.7200	-0.0010
7	4	4	6	4	3	5910.9070	-0.0011
7	4	3	6	4	2	5931.7170	-0.0063
8	1	8	7	1	7	6065.2270	0.0057
7	3	4	6	3	3	6070.5470	0.0034
8	2	7	7	2	6	6461.3793	-0.0016
8	1	7	7	1	6	6576.5753	0.0067
8	3	6	7	3	5	6706.1224	0.0009
9	0	9	8	0	8	6801.7038	-0.0070

Table S2.7. **II**-2W-**1**/**2**/**3** (OD-DOH-DOH) assigned transitions, along with their frequencies and deviation from the calculated value ($\Delta\nu = \nu - \nu_{calc}$).

J	K_a	K_c	J'	K_a'	K_c'	ν/ MHz	$\Delta\nu$/ MHz
3	1	3	2	1	2	2301.1488	-0.0003
3	0	3	2	0	2	2395.3328	-0.0048
4	2	2	3	2	1	3426.5759	0.0002
5	1	5	4	1	4	3791.5626	-0.0016
5	0	5	4	0	4	3845.5255	-0.0015
5	2	4	4	2	3	4067.2253	0.0012
5	1	4	4	1	3	4260.6249	-0.0049
6	1	6	5	1	5	4523.9506	0.0031
6	0	6	5	0	5	4555.0174	0.0039
6	2	5	5	2	4	4848.9815	0.0050
6	3	4	5	3	3	4982.2864	0.0040
6	4	3	5	4	2	4988.7182	-0.0043
6	4	2	5	4	1	4995.4335	-0.0007
6	3	3	5	3	2	5080.5780	0.0040
6	2	4	5	2	3	5216.2350	0.0049
7	1	7	6	1	6	5250.7250	-0.0007
7	0	7	6	0	6	5266.8260	0.0002
7	2	6	6	2	5	5616.2664	-0.0007
7	1	6	6	1	5	5773.6761	-0.0049
7	3	5	6	3	4	5805.0996	-0.0005
7	4	4	6	4	3	5833.0495	0.0010
7	4	3	6	4	2	5854.4558	-0.0016
8	1	8	7	1	7	5974.0269	-0.0017
8	0	8	7	0	7	5981.8271	-0.0017
7	3	4	6	3	3	5994.5513	-0.0031
7	2	5	6	2	4	6078.4783	-0.0011
8	2	7	7	2	6	6369.8207	-0.0005
8	1	7	7	1	6	6482.8409	0.0052

Table S2.8. **II**-2W-**1**/**2**/**3** (OD-DOH-HOH) assigned transitions, along with their frequencies and deviation from the calculated value ($\Delta\nu = \nu - \nu_{calc}$).

J	K_a	K_c	J'	K_a'	K_c'	ν/ MHz	$\Delta\nu$/ MHz
5	1	5	4	1	4	3821.2884	0.0022
5	1	4	4	1	3	4293.4691	0.0000
5	2	3	4	2	2	4365.1554	-0.0003
6	1	6	5	1	5	4559.1994	0.0035
6	0	6	5	0	5	4589.2092	-0.0049
6	2	5	5	2	4	4887.1378	0.0005

6	3	4	5	3	3	5023.4697	0.0053
6	1	5	5	1	4	5074.0015	-0.0047
6	2	4	5	2	3	5260.1022	-0.0004
7	1	7	6	1	6	5291.5244	0.0021
7	0	7	6	0	6	5306.8999	-0.0032
7	2	6	6	2	5	5659.8053	-0.0004
7	1	6	6	1	5	5814.6363	0.0042
7	4	4	6	4	3	5882.1796	-0.0041
7	4	3	6	4	2	5904.9672	0.0007
8	1	8	7	1	7	6020.4243	-0.0032
8	0	8	7	0	7	6027.7997	0.0009
8	2	7	7	2	6	6418.5652	0.0009
9	0	9	8	0	8	6750.8255	0.0012

Table S2.9. II-2W-**1**/**2**/**3** (OD-HOH-DOH) assigned transitions, along with their frequencies and deviation from the calculated value ($\Delta\nu = \nu - \nu_{calc}$).

J	K_a	K_c	J'	K_a'	K_c'	ν/ MHz	$\Delta\nu$/ MHz
4	1	4	3	1	3	3072.1561	0.0052
4	0	4	3	0	3	3153.4503	0.0019
4	2	3	3	2	2	3289.8292	-0.0070
4	2	2	3	2	1	3439.7279	-0.0005
5	1	5	4	1	4	3818.3488	0.0005
5	0	5	4	0	4	3874.3491	0.0010
5	2	3	4	2	2	4344.3383	-0.0001
6	1	6	5	1	5	4556.6492	0.0024
6	0	6	5	0	5	4589.4803	-0.0032
6	2	5	5	2	4	4878.2825	-0.0022
6	3	4	5	3	3	5007.4536	-0.0005
6	4	3	5	4	2	5012.7702	-0.0034
6	4	2	5	4	1	5018.8713	0.0013
6	1	5	5	1	4	5068.3091	0.0014
6	2	4	5	2	3	5237.9585	0.0020
7	1	7	6	1	6	5289.2944	0.0002
7	2	6	6	2	5	5651.8123	0.0006
7	1	6	6	1	5	5813.6394	0.0021
7	3	5	6	3	4	5835.4083	0.0002
7	5	3	6	5	2	5843.7417	0.0012
7	5	2	6	5	1	5844.5168	0.0006
7	4	3	6	4	2	5880.3649	0.0001
7	3	4	6	3	3	6015.4274	-0.0002
8	1	8	7	1	7	6018.3738	-0.0011
8	0	8	7	0	7	6026.9044	-0.0027

7	2	5	6	2	4	6106.7985	0.0000
8	2	7	7	2	6	6411.8332	-0.0006
8	1	7	7	1	6	6530.4023	-0.0018
9	1	9	8	1	8	6745.4261	-0.0002
9	0	9	8	0	8	6749.4441	0.0024
8	4	4	7	4	3	6760.1378	0.0003

Table S2.10. II-2W-**1/2/3** (OH-DOH-HOH) assigned transitions, along with their frequencies and deviation from the calculated value ($\Delta\nu = \nu - \nu_{calc}$).

J	K_a	K_c	J'	K_a'	K_c'	ν/ MHz	$\Delta\nu$/ MHz
4	1	4	3	1	3	3084.6268	-0.0018
4	0	4	3	0	3	3164.8617	0.0048
4	2	3	3	2	2	3304.8877	-0.0020
4	2	2	3	2	1	3458.8783	0.0044
5	1	5	4	1	4	3833.4258	0.0008
5	0	5	4	0	4	3887.9162	0.0002
5	2	4	4	2	3	4108.8009	0.0044
5	3	3	4	3	2	4192.4745	-0.0014
5	3	2	4	3	1	4232.3966	0.0019
5	2	3	4	2	2	4368.1648	0.0025
6	1	6	5	1	5	4574.2612	-0.0011
6	0	6	5	0	5	4605.7588	0.0004
6	2	5	5	2	4	4899.0667	-0.0010
6	3	4	5	3	3	5031.6748	-0.0012
6	4	3	5	4	2	5037.8756	0.0009
6	4	2	5	4	1	5044.4527	-0.0055
6	1	5	5	1	4	5087.7532	-0.0020
6	3	3	5	3	2	5128.8601	-0.0027
6	2	4	5	2	3	5265.2496	-0.0037
7	1	7	6	1	6	5309.4756	-0.0002
7	2	6	6	2	5	5674.9381	-0.0020
7	1	6	6	1	5	5833.5755	-0.0017
7	3	5	6	3	4	5862.9244	-0.0001
7	5	3	6	5	2	5872.9902	-0.0046
7	4	3	6	4	2	5911.3836	0.0088
7	3	4	6	3	3	6050.5993	-0.0010
7	2	5	6	2	4	6136.3222	0.0014
8	1	7	7	1	6	6551.5081	0.0015
9	1	9	8	1	8	6770.9403	-0.0007
9	0	9	8	0	8	6774.6446	0.0011
8	2	6	7	2	5	6972.0505	0.0015

Table S2.11. **II**-2W-**1**/**2**/**3** (OH-HOH-DOH) assigned transitions, along with their frequencies and deviation from the calculated value ($\Delta\nu = \nu - \nu_{calc}$).

J	***K_a***	***K_c***	***J'***	***K_a'***	***K_c'***	ν/ MHz	Δν/ MHz
3	1	3	2	1	2	2323.0253	-0.0007
3	0	3	2	0	2	2417.8376	0.0024
3	2	2	2	2	1	2482.2957	0.0056
4	1	4	3	1	3	3081.4440	0.0030
4	0	4	3	0	3	3163.9720	0.0030
4	2	3	3	2	2	3296.5160	0.0027
4	3	2	3	3	1	3338.6727	-0.0012
4	3	1	3	3	0	3349.3402	0.0025
4	2	2	3	2	1	3442.0994	0.0036
5	1	5	4	1	4	3830.5060	-0.0063
5	0	5	4	0	4	3888.2436	0.0029
5	4	1	4	4	0	4175.7758	-0.0042
5	3	3	4	3	2	4178.6244	0.0071
5	3	2	4	3	1	4214.3720	0.0001
5	1	4	4	1	3	4293.0320	0.0006
5	2	3	4	2	2	4347.3920	-0.0023
6	1	6	5	1	5	4571.7510	-0.0007
6	0	6	5	0	5	4606.1440	0.0031
6	2	5	5	2	4	4890.1880	-0.0009
6	3	4	5	3	3	5015.7400	-0.0002
6	4	3	5	4	2	5020.1420	-0.0040
6	4	2	5	4	1	5025.7450	-0.0031
6	1	5	5	1	4	5081.7410	-0.0002
6	3	3	5	3	2	5103.5580	-0.0004
7	1	7	6	1	6	5307.3120	-0.0008
7	0	7	6	0	6	5325.7290	0.0023
7	2	6	6	2	5	5666.8790	-0.0041
7	1	6	6	1	5	5832.2700	-0.0037
7	3	5	6	3	4	5845.8490	-0.0036
7	5	2	6	5	1	5853.0729	0.0024
7	4	4	6	4	3	5869.2390	0.0000
7	4	3	6	4	2	5887.1910	-0.0047
7	3	4	6	3	3	6017.7760	-0.0020
8	1	8	7	1	7	6039.2320	-0.0048
8	0	8	7	0	7	6048.4360	-0.0039
7	2	5	6	2	4	6115.1450	-0.0001
8	1	7	7	1	6	6553.5909	0.0030
8	5	4	7	5	3	6702.0517	0.0017
8	5	3	7	5	2	6704.7607	-0.0003

8	4	4	7	4	3	6765.9492	0.0073
9	1	9	8	1	8	6769.0658	0.0064
9	0	9	8	0	8	6773.4504	-0.0009

Table S2.12. **II**-2W-**1**/**2**/**3** (OH-HOD-HOH) assigned transitions, along with their frequencies and deviation from the calculated value (Δν = ν - ν_{calc}).

J	K_a	K_c	***J'***	K_a'	K_c'	ν/ MHz	Δν/ MHz
3	1	3	2	1	2	2317.4076	-0.0062
3	1	2	2	1	1	2627.0759	-0.0036
4	0	4	3	0	3	3149.5426	0.0057
4	2	3	3	2	2	3297.5448	0.0036
4	2	2	3	2	1	3460.5002	-0.0026
5	1	5	4	1	4	3816.4689	-0.0005
5	0	5	4	0	4	3867.4895	-0.0036
5	2	4	4	2	3	4098.0129	0.0019
5	1	4	4	1	3	4291.6698	0.0044
5	2	3	4	2	2	4369.6344	0.0014
6	1	6	5	1	5	4552.9079	0.0045
6	0	6	5	0	5	4581.4599	0.0036
6	2	5	5	2	4	4883.9999	0.0018
6	3	4	5	3	3	5024.1684	0.0014
6	4	3	5	4	2	5032.5036	-0.0018
6	4	2	5	4	1	5040.2865	-0.0041
7	1	7	6	1	6	5283.7883	-0.0084
7	0	7	6	0	6	5298.2001	-0.0003
7	2	6	6	2	5	5654.8783	-0.0046
7	1	6	6	1	5	5805.6995	-0.0037
7	3	5	6	3	4	5852.3849	0.0020
7	5	3	6	5	2	5866.6949	-0.0016
7	5	2	6	5	1	5867.7684	0.0038
7	4	4	6	4	3	5884.4963	0.0036
7	4	3	6	4	2	5909.2131	-0.0027
8	1	8	7	1	7	6011.3509	0.0046

Table S2.13. **II**-2W-**1**/**2**/**3** (OH-DOH-DOH) assigned transitions, along with their frequencies and deviation from the calculated value (Δν = ν - ν_{calc}).

J	K_a	K_c	***J'***	K_a'	K_c'	ν/ MHz	Δν/ MHz
3	1	3	2	1	2	2307.5772	0.0052
3	0	3	2	0	2	2402.0377	-0.0004
4	1	4	3	1	3	3060.2757	0.0032

4	0	4	3	0	3	3141.2895	-0.0030
4	2	3	3	2	2	3278.2478	-0.0025
4	2	2	3	2	1	3428.7865	0.0004
4	1	3	3	1	2	3452.2395	0.0006
5	1	5	4	1	4	3803.4262	0.0060
5	0	5	4	0	4	3859.0753	-0.0035
5	2	4	4	2	3	4076.0961	0.0064
5	3	3	4	3	2	4157.7908	0.0081
5	3	2	4	3	1	4196.0047	-0.0039
6	1	6	5	1	5	4538.6662	0.0023
6	0	6	5	0	5	4571.2106	-0.0001
6	2	5	5	2	4	4860.6063	-0.0083
6	3	4	5	3	3	4990.3189	-0.0010
6	4	3	5	4	2	4995.7913	-0.0054
6	4	2	5	4	1	5001.9813	0.0029
6	1	5	5	1	4	5050.2127	-0.0042
6	3	3	5	3	2	5083.7092	0.0005
6	2	4	5	2	3	5221.2073	-0.0013
7	1	7	6	1	6	5268.2657	-0.0004
7	0	7	6	0	6	5285.3865	-0.0004
5	2	3	4	1	3	5391.4943	-0.0014
4	3	2	3	2	2	5482.6256	0.0019
7	2	6	6	2	5	5631.0165	-0.0016
7	1	6	6	1	5	5792.0859	-0.0059
7	3	5	6	3	4	5815.2833	-0.0002
7	5	3	6	5	2	5823.9233	-0.0037
7	5	2	6	5	1	5824.7187	0.0016
7	4	4	6	4	3	5841.0899	0.0012
7	4	3	6	4	2	5860.8512	-0.0012
7	3	4	6	3	3	5996.5959	0.0005
8	0	8	7	0	7	6002.7316	0.0012
7	2	5	6	2	4	6086.8254	0.0030
8	2	7	7	2	6	6387.8867	-0.0022
8	1	7	7	1	6	6505.5557	0.0051
8	4	5	7	4	4	6687.4124	0.0048
9	1	9	8	1	8	6718.3523	-0.0003
9	0	9	8	0	8	6722.3027	0.0002
8	2	6	7	2	5	6918.2531	-0.0022
8	3	5	7	3	4	6921.1744	0.0013

Table S3.1. Experimental spectroscopic constants for the PhTFE(OH) **II**···DOD species.[a]

Constants	(OH) **II**···DOD
A/ MHz	1048.1823(81)
B/ MHz	557.13058(46)
C/ MHz	453.70015(38)
Δ_K/ kHz	[0. 9052]
Δ_{JK}/ kHz	0.105(25)
Δ_J/ kHz	0.0254(51)
δ_K/ kHz	[-0.0703]
δ_J/ kHz	[0.00839]
σ/ kHz	3.8
N	22

[a] Standard errors in units of the least significant digit can be found enclosed within parentheses next to their respective fit parameter. The quartic centrifugal distortion constants within square parentheses were held fixed at the B3LYP-D3BJ/def2-TZVPD predicted values of the parent species (see reference 7). σ is the standard deviation of the fit in kHz and *N* is the number of rotational transitions included in the fit.

Table S3.2. PhTFE(OH) **II**···DOD assigned transitions, along with their frequencies and deviation from the calculated value ($\Delta\nu = \nu - \nu_{calc}$).

J	K_a	K_c	***J'***	K_a'	K_c'	ν/ MHz	Δν/ MHz
3	1	3	2	1	2	2868.7415	0.0050
4	1	4	3	1	3	3810.6248	-0.0075
4	2	3	3	2	2	4031.8317	-0.0033
4	3	1	3	3	0	4076.9473	0.0086
4	2	2	3	2	1	4163.6471	0.0046
5	1	5	4	1	4	4743.5199	0.0013
5	0	5	4	0	4	4821.4644	-0.0024
5	2	4	4	2	3	5021.5631	0.0007
5	3	3	4	3	2	5092.2921	0.0019
5	3	2	4	3	1	5118.8128	-0.0045
5	1	4	4	1	3	5234.1288	-0.0012
6	1	6	5	1	5	5668.2971	-0.0034
6	0	6	5	0	5	5719.9257	-0.0036
6	2	5	5	2	4	5999.7968	0.0004
6	4	3	5	4	2	6113.8019	0.0005
6	3	4	5	3	3	6114.2948	-0.0013
6	4	2	5	4	1	6117.2427	-0.0033
6	3	3	5	3	2	6181.1692	-0.0012
6	1	5	5	1	4	6221.9334	0.0029
6	2	4	5	2	3	6341.3815	-0.0032
7	0	7	6	0	6	6617.3163	0.0075
7	1	6	6	1	5	7173.7123	-0.0008
3	1	3	2	1	2	2868.7415	0.0050

4	1	4	3	1	3	3810.6248	-0.0075
4	2	3	3	2	2	4031.8317	-0.0033
4	3	1	3	3	0	4076.9473	0.0086
4	2	2	3	2	1	4163.6471	0.0046
5	1	5	4	1	4	4743.5199	0.0013
5	0	5	4	0	4	4821.4644	-0.0024
5	2	4	4	2	3	5021.5631	0.0007
5	3	3	4	3	2	5092.2921	0.0019
5	3	2	4	3	1	5118.8128	-0.0045
5	1	4	4	1	3	5234.1288	-0.0012
6	1	6	5	1	5	5668.2971	-0.0034
6	0	6	5	0	5	5719.9257	-0.0036
6	2	5	5	2	4	5999.7968	0.0004
6	4	3	5	4	2	6113.8019	0.0005
6	3	4	5	3	3	6114.2948	-0.0013
6	4	2	5	4	1	6117.2427	-0.0033
6	3	3	5	3	2	6181.1692	-0.0012
6	1	5	5	1	4	6221.9334	0.0029
6	2	4	5	2	3	6341.3815	-0.0032
7	0	7	6	0	6	6617.3163	0.0075
7	1	6	6	1	5	7173.7123	-0.0008

Table S4. Predicted rotational and quartic centrifugal distortion constants for **II**-2W-**1**, **II**-2W-**2**, and **II**-2W-**3** calculated at the B3LYP-D3BJ/def2-TZVPPD level of theory along with the experimental constants for **II**-2W-**1**/**2**/**3**.

	Experiment	**B3LYP-D3BJ**		
Constants	**II**-2W-**1**/**2**/**3**	**II**-2W-**1**	**II**-2W-**2**	**II**-2W-**3**
A/ MHz	851.12402(20)	852.8	856.8	864.8
B/ MHz	467.4997798(79)	468.6	464.8	468.0
C/ MHz	366.804747(82)	364.4	366.4	368.5
Δ_K/ kHz	0.520(12)	0.537	0.605	0.546
Δ_{JK}/ kHz	-0.0766(16)	-0.111	-0.132	-0.121
Δ_J/ kHz	0.03740(63)	0.040	0.038	0.042
δ_K/ kHz	[0.008694]	0.009	-0.014	0.013
δ_J/ kHz	0.01038(28)	0.013	0.012	0.014

Table S5. Comparison of the calculated Cartesian coordinates in the principal axis system for **II**-2W-**1**, **II**-2W-**2**, and **II**-2W-**3** with the experimental substitution coordinates for **II**-2W-**1**/**2**/**3** obtained from the isotopic substitution analysis for multiply substituted species. In this table, single, and double isotopically substituted species were used as the parent species for the Kraitchman analysis of doubly and triply substituted species, respectively.[a]

Parent Species	**Substituted Species**	**Experimental Substitution Coordinates**		
		a	***b***	***c***
D13	H21	-1.9383(9)	2.6206(7)	-0.384(5)
	H24	-3.1989(5)	0.885(2)	1.015*i(2)
D21	H13	0.546(4)	2.1662(9)	0.474(4)
	H24	-3.1979(5)	0.959(2)	1.097*i(2)
D24	H13	0.561(3)	2.1692(8)	0.489(3)
	H21	-1.9412(9)	2.6492(6)	0.099*i(17)
D21 and D24	H13	0.546(3)	2.1585(8)	0.486(4)
^{18}O20	O23	-3.4370(1)	1.3123(4)	-0.215(2)
^{18}O23	O20	-1.2361(5)	3.0763(2)	-0.194(3)

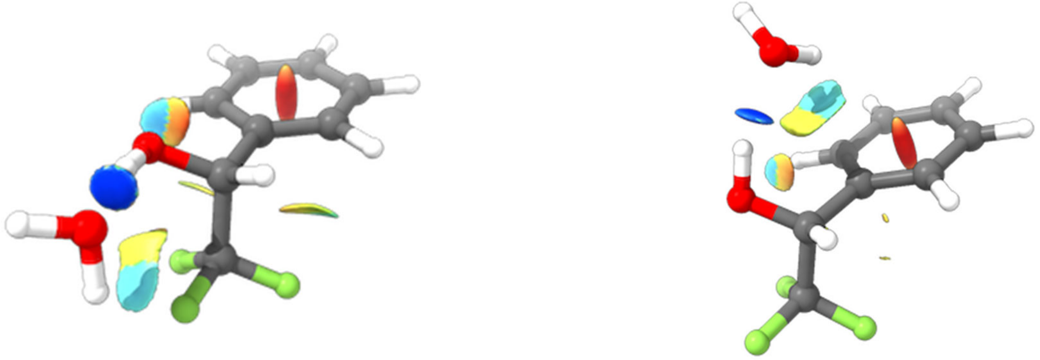
Parent Species	**Substituted Species**	**II-2W-1/2/3 Predicted Coordinates**		
		a	***b***	***c***
D13	H21	-2.09 / -2.10 / -2.03	2.58 / 2.54 / 2.59	-0.27 / -0.22 / -0.21
	H24	-3.03 / -2.99 / -3.10	0.63 / 0.48 / 0.63	0.41 / -0.71 / -0.52
D21	H13	0.13 / 0.15 / 0.48	2.27 / 2.25 / 2.26	0.30 / 0.48 / 0.50
	H24	-3.03 / -2.99 / -3.10	0.63 / 0.48 / 0.63	0.41 / -0.71 / -0.52
D24	H13	0.13 / 0.15 / 0.48	2.27 / 2.25 / 2.26	0.30 / 0.48 / 0.50
	H21	-2.09 / -2.10 / -2.03	2.58 / 2.54 / 2.59	-0.27 / -0.22 / -0.21
D21 and D24	H13	0.13 / 0.15 / 0.48	2.27 / 2.25 / 2.26	0.30 / 0.48 / 0.50
^{18}O20	O23	-3.43 / -3.41 / -3.40	1.40 / 1.34 / 1.42	-0.02 / -0.55 / -0.06
^{18}O23	O20	-1.28 / -1.34 / -1.19	3.11 / 3.10 / 3.08	-0.41 / 0.01 / -0.30

[a] Costain errors on experimental values are included in the parentheses next to the coordinate and are in units of the last digit. Coordinates with imaginary numbers indicate that the value is near zero. Theoretical coordinates of **II**-2W-**1**, **II**-2W-**2**, and **II**-2W-**3** in their principal axis orientation in the specific parent species are provided for the three lowest energy structures, where the coordinate for each conformer is separated by a slash. All coordinates are in units of Å.

III-2W-**12** (slight distortion) **III**-2W-**15** (significant distortion)

Figure S2. Sample molecular models showing complexes containing monomeric PhTFE **III** being only slightly (**III**-2W-**12**) and significantly distorted (**III**-2W-**15**).

PhTFE **I** PhTFE **II**



I – W1 **II** – W3

Figure S3. NCI analyses for the two lowest energy PhTFE monomer conformers and the two most relevant PhTFE monohydrate conformers, calculated at the B3LYP-D3BJ/def2-TZVPPD level of theory. The value (from -0.050 to 0.050) of sign(λ_2)ρ at a particular point is used to colour the RDG surface (isosurface 0.60). Colour gradient goes from blue (stabilizing) to red (destabilizing), with weak interactions being indicated by green.