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Journal Name

ARTICLE

Microwave Spectrum of the Strongly Hydrogen Bonded Hexafluoroisopropanol•••Water Complex

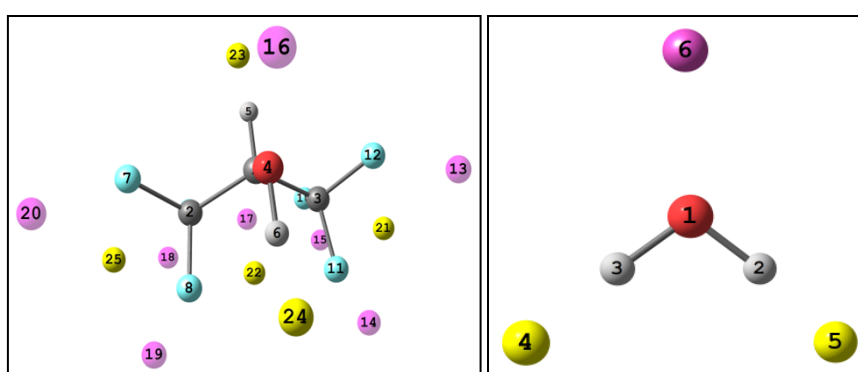A. Shahi, E. Arunan

Supporting Information

Figure S1. ESP minima (pink spheres) and maxima (yellow spheres) are shown for HFIP (left) and water (right). Coordinate of these molecules and the maxima/minima points are given in the Table S1-S4.

Table S1. ESP maxima and minima for HFIP at LC-wPBE/6-311++G**. Starred points are the extreme values in the set of maxima or minima.

	# (label)	kJ/mol	X (Å)	Y (Å)	Z (Å)

	# (label)	kJ/mol	X (Å)	Y (Å)	Z (Å)
	13	-27.17	-3.91	0.66	-0.15
	14	-23.41	-2.25	-0.97	2.36
	15	-25.50	-1.94	-2.76	0.46
*	16	-78.17	-0.05	3.33	-1.23
	17	-28.84	-0.07	-2.63	-0.22
	18	-25.50	1.97	-2.76	0.44
	19	-23.41	2.25	-0.96	2.37
	20	-27.17	3.87	0.81	-0.10

ESP maxima and minima values for HFIP
Number of surface minima: 8

Number of surface maxima: 5

	# (label)	kJ/mol	X (Å)	Y (Å)	Z (Å)
	21	62.7	-2.90	-0.93	0.56
	22	84.02	0.03	-1.37	1.10
	23	149.64	0.05	0.15	-2.88
*	24	235.75	-0.07	2.28	1.90
	25	62.28	2.92	-0.91	0.55

Table S2. ESP maxima and minima for water at LC-wPBE/6-311++G**. Starred points are the extreme values in the set of maxima or minima.

	ESP maxima and minima values for Water			
	Number of surface minima: 1			
# (label)	kJ/mol	X (Å)	Y (Å)	Z (Å)
* 6	-160.51	-0.05	1.96	0.05
	Number of surface maxima: 2			
* 4	191.86	-1.68	-1.25	0.03
5	191.44	1.62	-1.31	-0.04

Table S3. Coordinate of HFIP at LC-wPBE/6-311++G**

	Coordinate of the HFIP molecule		
Atoms	X (Å)	Y (Å)	Z (Å)
C	0.00	0.52	-0.53
C	1.29	-0.15	-0.04
C	-1.29	-0.15	-0.04
O	0.00	1.86	-0.18
H	0.00	0.46	-1.62
H	0.00	1.95	0.78
F	2.34	0.44	-0.61
F	1.42	-0.02	1.29
F	1.33	-1.45	-0.34
F	-1.33	-1.45	-0.34
F	-1.42	-0.02	1.29
F	-2.34	0.44	-0.61

Table S4. Coordinate of the water molecule at LC-wPBE/6-311++G**

	Coordinate of water molecule		
Atoms	X (Å)	Y (Å)	Z (Å)
O	0.00	0.12	0.00
H	0.76	-0.46	0.00
H	-0.76	-0.46	0.00

Table S5. Comparison between absolute Gibbs free energy and change in Gibbs free energy on complex formation. All calculations are reported at MP2/6-311++G(d,p) level of theory. Enthalpy is treated in the same manner.

Structure	Total Gibbs free Energy (Hartree)	Relative Gibbs free energy (kJ mol^{-1})	Relative change in Gibbs free energy (kJ mol^{-1})
2a	-864.558704	0.0	0.0
2b	-864.553752	13.0	13.0
2c	-864.558469	0.6	-2.9
	Total Enthalpy (Hartree)	Relative Enthalpy (kJ mol-1)	Relative change in Enthalpy (kJ mol-1)
2a	-864.558096	0	0.0
2b	-864.553143	13.0	13.0
2c	-864.55786	0.6	-3.0

Table S6. Observed rotational transitions for the HFIP•••H$_2$O complex.

J, K$_{-1}$, K$_{+1}$ <- J, K$_{-1}$, K$_{+1}$	Type	Observed (MHz)	Obs-Calc (MHz)
2, 0, 2 <- 1, 1, 1	b	3062.6515	-0.0029
2, 1, 2 <- 1, 0, 1	b	3250.3360	0.0080
3, 0, 3 <- 2, 1, 2	b	4556.3460	0.0031
3, 1, 3 <- 2, 0, 2	b	4607.4975	0.0089
4, 0, 4 <- 3, 1, 3	b	5987.3295	-0.0025
4, 1, 4 <- 3, 0, 3	b	5996.9975	-0.0008
5, 0, 5 <- 4, 1, 4	b	7401.5900	-0.0005
5, 1, 5 <- 4, 0, 4	b	7403.1100	-0.0069
5, 2, 4 <- 4, 1, 3	b	8139.8660	0.0052
5, 2, 3 <- 4, 3, 2	b	8434.5610	0.0015
4, 4, 1 <- 3, 3, 0	b	8760.1525	-0.0008
4, 4, 0 <- 3, 3, 0	c	8799.4635	-0.0050
6, 0, 6 <- 5, 1, 5	b	8812.6180	0.0044
6, 1, 6 <- 5, 0, 5	b	8812.8320	-0.0001
4, 4, 1 <- 3, 3, 1	c	8852.7780	-0.0031
4, 3, 1 <- 3, 2, 2	b	8988.1890	-0.0072
5, 3, 3 <- 4, 2, 2	b	9126.4780	-0.0030
6, 1, 5 <- 5, 2, 4	b	9507.5520	-0.0004
6, 2, 5 <- 5, 1, 4	b	9521.1735	-0.0104
6, 2, 4 <- 5, 3, 3	b	10103.4265	0.0029
7, 0, 7 <- 6, 1, 6	b	10223.1295	-0.0038
7, 1, 7 <- 6, 0, 6	b	10223.1685	0.0058
5, 4, 2 <- 4, 3, 1	b	10257.7875	0.0013
5, 3, 2 <- 4, 2, 2	c	10264.5755	-0.0022
6, 3, 4 <- 5, 2, 3	b	10354.0435	0.0022
5, 2, 3 <- 4, 1, 3	c	10397.9045	-0.0002
5, 1, 4 <- 4, 0, 4	c	10516.2925	0.0016
5, 4, 1 <- 4, 3, 1	c	10523.6245	-0.0001
5, 2, 4 <- 4, 1, 4	c	10526.5365	0.0058
5, 3, 3 <- 4, 2, 3	c	10539.2920	0.0022
5, 4, 2 <- 4, 3, 2	c	10715.2270	0.0041
7, 1, 6 <- 6, 2, 5	b	10922.3905	-0.0010
7, 2, 6 <- 6, 1, 5	b	10924.7730	-0.0064
5, 4, 1 <- 4, 3, 2	b	10981.0705	0.0064
5, 5, 1 <- 4, 4, 0	b	11066.9635	0.0009
5, 5, 0 <- 4, 4, 0	c	11081.8605	0.0032
5, 5, 1 <- 4, 4, 1	c	11106.2760	-0.0018
5, 5, 0 <- 4, 4, 1	b	11121.1725	0.0000
8, 0, 8 <- 7, 1, 7	b	11633.5880	0.0019
8, 1, 8 <- 7, 0, 7	b	11633.5880	-0.0019
7, 3, 4 <- 6, 4, 3	b	12015.0996	0.0000
8, 1, 7 <- 7, 2, 6	b	12333.2535	0.0002
8, 2, 7 <- 7, 1, 6	b	12333.6345	0.0016
9, 0, 9 <- 8, 1, 8	b	13044.0270	0.0005
9, 1, 9 <- 8, 0, 8	b	13044.0270	0.0001
10, 0, 10 <- 9, 1, 9	b	14454.4560	0.0002
10, 1, 10 <- 9, 0, 9	b	14454.4560	0.0001

Table S7. Observed rotational transitions for the HFIP•••D_2O complex.

J, K_{-1}, K_{+1} <- J, K_{-1}, K_{+1}	Type	Observed (MHz)	Obs-Calc (MHz)
4, 0, 4 <- 3, 1, 3	b	5810.5170	-0.0016
4, 1, 4 <- 3, 0, 3	b	5813.0460	0.0010
5, 0, 5 <- 4, 1, 4	b	7178.7880	-0.0010
5, 1, 5 <- 4, 0, 4	b	7179.0490	-0.0005
5, 2, 4 <- 4, 1, 3	b	7874.8170	0.0069
6, 0, 6 <- 5, 1, 5	b	8546.1100	-0.0051
6, 1, 6 <- 5, 0, 5	b	8546.1390	-0.0004
6, 1, 5 <- 5, 2, 4	b	9230.7850	-0.0027
6, 2, 5 <- 5, 1, 4	b	9233.1410	0.0003
7, 0, 7 <- 6, 1, 6	b	9913.3510	0.0023
7, 1, 7 <- 6, 0, 6	b	9913.3510	0.0001
8, 0, 8 <- 7, 1, 7	b	11280.5705	0.0009
8, 1, 8 <- 7, 0, 7	b	11280.5705	0.0007
7, 2, 5 <- 6, 3, 4	b	11281.7270	0.0030
7, 3, 5 <- 6, 2, 4	b	11293.4195	-0.0023
5, 3, 2 <- 4, 2, 2	c	10083.8165	0.0017
5, 5, 0 <- 4, 4, 1	b	10621.2490	0.0046
7, 1, 6 <- 6, 2, 5	b	10598.5855	0.0040
7, 2, 6 <- 6, 1, 5	b	10598.8510	0.0014
5, 5, 1 <- 4, 4, 0	b	10499.0430	-0.0003
5, 1, 4 <- 4, 2, 3	b	7857.0490	-0.0022
6, 6, 0 <- 5, 5, 1	b	12739.5975	-0.0037
4, 4, 0 <- 3, 3, 1	b	8528.5805	-0.0061
9, 0, 9 <- 8, 1, 8	b	12647.7785	-0.0008
9, 1, 9 <- 8, 0, 8	b	12647.7785	-0.0008
8, 2, 6 <- 7, 3, 5	b	12651.9490	-0.0068
8, 3, 6 <- 7, 2, 5	b	12653.5610	0.0024
6, 6, 1 <- 5, 5, 0	b	12679.7318	0.0028
9, 1, 8 <- 8, 2, 7	b	13332.7780	0.0019
9, 2, 8 <- 8, 1, 7	b	13332.7780	-0.0008

ARTICLE

Table S8. Observed rotational transitions for the HFIP•••HOD complex.

$J, K_{-1}, K_{+1} <- J, K_{-1}, K_{+1}$	Type	Observed (MHz)	Obs-Calc (MHz)
4, 0, 4 <- 3, 1, 3	b	5917.0530	-0.0002
4, 1, 4 <- 3, 0, 3	b	5923.2175	0.0042
5, 0, 5 <- 4, 1, 4	b	7312.9070	0.0022
5, 2, 4 <- 4, 1, 3	b	8030.5025	-0.0001
4, 4, 1 <- 3, 3, 1	c	8684.1000	0.0038
6, 0, 6 <- 5, 1, 5	b	8706.6000	-0.0009
6, 1, 6 <- 5, 0, 5	b	8706.7025	-0.0031
4, 4, 0 <- 3, 3, 1	b	8735.5610	-0.0062
6, 1, 5 <- 5, 2, 4	b	9396.5805	0.0006
6, 2, 5 <- 5, 1, 4	b	9404.1610	0.0034
7, 0, 7 <- 6, 1, 6	b	10100.0100	0.0001
7, 1, 7 <- 6, 0, 6	b	10100.0100	-0.0121
6, 3, 4 <- 5, 2, 3	b	10187.6340	-0.0005
7, 1, 6 <- 6, 2, 5	b	10792.2780	0.0028
7, 2, 6 <- 6, 1, 5	b	10793.4310	0.0067
5, 5, 1 <- 4, 4, 0	b	10836.4875	0.0038
5, 5, 0 <- 4, 4, 0	c	10858.0510	0.0002
5, 4, 1 <- 4, 3, 2	b	10878.3150	0.0003
5, 5, 1 <- 4, 4, 1	c	10887.9485	-0.0062
5, 5, 0 <- 4, 4, 1	b	10909.5245	0.0027
8, 0, 8 <- 7, 1, 7	b	11493.3855	0.0019
8, 1, 8 <- 7, 0, 7	b	11493.3855	0.0006
9, 1, 9 <- 8, 0, 8	b	12886.7470	0.0016
9, 0, 9 <- 8, 1, 8	b	12886.7470	0.0018
9, 2, 7 <- 8, 3, 6	b	14272.7320	-0.0031
9, 3, 7 <- 8, 2, 6	b	14273.8295	-0.0006
10, 1, 10 <- 9, 0, 9	b	14280.0900	-0.0026
10, 0, 10 <- 9, 1, 9	b	14280.0900	-0.0026
10, 1, 9 <- 9, 2, 8	b	14972.0880	-0.0008
10, 2, 9 <- 9, 1, 8	b	14972.0880	-0.0033
7, 7, 1 <- 6, 6, 0	b	15308.1415	-0.0023
7, 7, 0 <- 6, 6, 0	c	15311.2610	-0.0075
7, 7, 1 <- 6, 6, 1	c	15316.5590	0.0066
7, 7, 0 <- 6, 6, 1	b	15319.6805	0.0033
10, 3, 8 <- 9, 2, 7	b	15665.6685	0.0024
11, 0, 11 <- 10, 1, 10	b	15673.4240	0.0024
11, 1, 11 <- 10, 0, 10	b	15673.4240	0.0024

Table S9. Observed rotational transitions for the HFIP(OD)•••H$_2$O complex.

$J, K_{-1}, K_{+1} <- J, K_{-1}, K_{+1}$	Type	Observed (MHz)	Obs-Calc (MHz)
4, 0, 4 <- 3, 1, 3	b	5966.1830	0.0030
4, 1, 4 <- 3, 0, 3	b	5974.6100	0.0017
5, 0, 5 <- 4, 1, 4	b	7374.9050	-0.0061
5, 1, 5 <- 4, 0, 4	b	7376.1780	-0.0048
6, 0, 6 <- 5, 1, 5	b	8780.7740	0.0024
6, 1, 6 <- 5, 0, 5	b	8780.9500	0.0049
5, 5, 1 <- 4, 4, 0	b	10989.2730	0.0001
5, 5, 0 <- 4, 4, 1	b	11048.6365	-0.0001
8, 1, 8 <- 7, 0, 7	b	11591.5830	-0.0018
8, 0, 8 <- 7, 1, 7	b	11591.5830	0.0009