

Support Information

Binary Conformers of a Flexible, Long-chain Fluoroalcohol: Dispersion

Controlled Selectivity and Relative Abundances in a Jet

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Table S1. Theoretical spectroscopic parameters of the 102 conformers of the TFB dimer calculated at the B3LYP-D3BJ/def2-TZVP level of theory.^a

Conformers	Energy ordering	ΔE	ΔE_0	<i>A</i>	<i>B</i>	<i>C</i>	$ \mu_a $	$ \mu_b $	$ \mu_c $
I(TG-g-/TG+g+)	1	0.0	0.0	565	299	272	1.1	1.8	1.3
II(TG+g+/TG+g+)	2	2.2	1.2	539	281	234	0.5	3.4	2.0
III(G-G-g+/TG-g-)	3	1.6	1.6	608	280	269	0.5	1.2	1.1
IV(TG-g-/TG+t)	4	3.2	1.8	512	320	257	0.9	5.0	2.1
V(TG+t/TG+t)	5	4.2	2.4	636	247	196	6.7	3.3	0.2
VI(TG-g-/TG+g+)	6	3.8	2.6	555	249	202	0.1	2.9	0.5
VII(TG-g-/G-G-t)	7	3.1	2.8	614	302	265	0.1	2.2	0.9
VIII(TG-g-/G+G+g-)	8	2.7	2.8	823	199	180	0.0	0.9	0.0
IX(TG-g-/G-G-g+)	9	2.8	3.0	604	323	263	0.4	2.5	0.1
X(G+G+g-/G-G-t)	10	2.8	3.0	679	268	264	0.3	0.6	1.3
XI(TG-g-/TG-t)	11	4.8	3.4	763	195	186	2.4	1.1	1.4
XII(G+G+g-/TG-g-)	12	3.5	3.5	788	206	195	1.4	1.7	1.0
XIII(TG-g-/TTg-)	13	3.4	3.5	515	312	233	0.7	3.0	2.0
XIV(G+G+t/TG-g-)	14	4.5	3.6	567	290	243	0.0	3.1	0.9
XV(TG-g-/G+G+t)	15	4.7	3.6	818	230	216	0.7	1.2	0.2
XVI(TG-g-/G-G-g+)	16	2.9	3.6	604	252	204	0.4	0.7	0.3
TG-g-/G+G+t ^b	17	4.9	3.8	589	267	223	0.1	3.4	2.1
TG-g-/TG-g+	18	5.0	4.1	541	337	265	0.8	1.5	1.5
TG-t/TG+t	19	4.6	4.1	577	231	189	5.8	3.8	0.1
TG+g+/TG-t	20	5.6	4.1	1007	156	145	2.6	0.7	0.2
TG-t/TG+t	21	5.0	4.2	686	197	166	5.6	5.0	0.2
TG-g-/TG-g-	22	6.3	4.3	681	239	234	0.3	1.5	0.3
G+G+t/TG+t	23	4.7	4.3	548	313	253	1.2	4.7	1.0
TG-g-/TG-t	24	5.9	4.3	1006	160	148	1.8	1.4	0.4
TG-g-/TG-t	25	5.2	4.4	528	292	242	1.9	3.9	2.7
G+G+g-/TG-g-	26	5.9	4.4	750	220	207	1.2	1.8	0.7
TG-g-/G-G-g+	27	4.3	4.5	568	300	222	0.3	2.0	0.5
G+G+g-/G+G+g-	28	4.6	4.5	712	259	237	0.0	2.0	0.4
G+G+g-/TG+t	29	3.6	4.5	991	172	157	2.3	1.9	0.6
TG-t/TG+t	30	5.5	4.6	603	265	202	6.3	4.0	1.7
TG-g-/TG+t	31	6.8	4.7	742	185	172	1.9	3.2	1.6
G+G+g-/TG+t	32	6.2	4.7	881	184	170	1.8	1.7	1.0
TG-g+/G-G-g+	33	5.4	4.9	870	205	186	0.4	0.8	0.2
TG-g-/G+G+t	34	4.7	4.9	759	197	176	1.2	1.9	1.6
G+G+t/G+G+g-	35	6.5	5.0	673	254	216	0.4	1.6	0.7
TG-g-/G+G+g+	36	4.6	5.0	735	229	213	2.4	0.8	0.5
TG-g-/TTg+	37	5.0	5.1	585	248	192	0.4	3.1	0.0
TG-g+/TG-t	38	7.0	5.1	588	267	260	0.8	3.8	2.9
TG-g-/TG-g-	39	6.7	5.2	740	170	151	2.2	1.0	0.4
TG+g-/TG-g-	40	6.2	5.2	588	252	241	1.3	2.0	2.8
TG+g+/G+G+g+	41	6.5	5.3	560	315	264	2.2	4.1	1.5
G+G+g-/G-G-g+	42	5.9	5.3	963	208	191	0.6	0.2	0.2
TG+t/TG+g+	43	4.4	5.4	559	244	191	4.9	3.0	0.9
G-G-g+/TG+t	44	7.7	5.5	937	179	165	2.9	1.2	0.9
TG-g-/G-Tg-	45	6.2	5.5	578	266	204	0.8	2.4	0.3
TG+t/TG+t	46	6.3	5.6	689	176	154	4.9	4.9	1.0
TG+t/TG-g-	47	7.4	5.7	581	241	186	5.3	3.4	1.3
TG+t/G-G-g+	48	7.3	5.7	790	152	137	2.5	2.6	0.2
G-G-g+/TG-g-	49	6.2	5.7	701	232	224	1.6	1.6	2.4
TG-g-/G+G+t	50	5.9	5.8	886	173	158	2.0	1.4	0.5
TG-g-/TG+g+	51	6.3	5.8	532	299	211	0.6	4.0	0.9
TG+g+/TTg+	52	7.9	5.8	611	237	208	1.1	1.3	1.4

TG+t/G-G-t	53	6.4	6.0	713	235	197	5.8	2.4	0.6
G-G-t/TG-g-	54	7.0	6.1	601	241	205	0.2	3.0	0.6
TG+g+/TG-g+	55	7.6	6.1	547	294	245	0.8	0.8	1.0
TG+g+/TG-g-	56	7.2	6.2	738	167	149	1.8	1.4	2.3
TG+g-/TG+g+	57	7.2	6.2	628	257	200	1.1	2.7	0.9
TG+g+/G-Tg-	58	7.8	6.4	612	236	188	0.4	1.7	2.3
G-G-g+/TG+t	59	8.1	6.4	624	269	245	0.6	2.2	2.1
TG+g+/G-G+g-	60	7.4	6.5	578	307	246	1.9	0.1	1.3
TG+g-/G-G+g-	61	6.9	6.5	732	207	181	1.6	1.1	0.6
TG-t/TG+g+	62	7.3	6.6	701	159	141	3.8	3.9	1.4
G-G-g+/TG+g+	63	9.2	6.7	722	244	201	0.8	2.1	0.3
TG+t/TG+g+	64	7.7	6.7	689	162	141	4.1	4.7	0.9
G+G+g-/TG-g-	65	8.7	6.8	857	166	151	2.1	0.2	1.5
TG-g+/TG-g-	66	7.8	6.8	516	299	245	0.4	3.4	1.9
G-G-g+/TG-g-	67	9.0	6.9	785	169	151	1.5	1.1	0.7
G+G+g-/G-G-g+	68	7.6	6.9	717	276	225	0.5	0.6	2.1
TG+g+/TG+g+	69	6.9	7.0	521	273	200	1.0	3.9	0.5
TG-g-/G+G+g-	70	9.3	7.1	596	297	226	0.7	1.8	2.5
TG-g-/G+G+g+	71	7.7	7.1	994	158	147	3.3	2.9	0.9
TG-g-/G-G-t	72	8.0	7.2	909	168	154	1.3	1.6	2.0
TG+t/G-G-t	73	7.7	7.2	840	140	128	2.6	4.7	0.3
TG+g+/TTt	74	10.1	7.5	913	155	145	2.5	0.7	0.0
TG+g+/TG+g+	75	8.6	7.5	549	343	270	0.0	0.0	0.1
TG+g-/G-G-g+	76	9.7	7.5	898	159	154	1.9	2.2	2.1
TG+t/G+G+t	77	7.7	7.5	643	203	172	2.6	4.2	2.2
TG+t/G+G+t	78	9.8	7.5	900	137	129	2.8	3.6	0.8
TG-g+/TG-g-	79	9.5	7.5	723	205	195	1.7	0.7	1.9
TG-g-/G-G-g-	80	8.5	7.6	622	272	255	0.7	1.5	1.8
TG+g+/TTt	81	8.7	7.7	508	279	216	0.4	2.3	1.7
TG+g-/TG+g+	82	9.2	7.7	550	252	195	1.0	3.6	0.3
TTt/TG+t	83	9.6	7.7	667	224	184	6.3	3.3	1.7
TG+t/G+G+t	84	10.0	7.8	793	189	168	5.1	3.5	0.8
TG-t/TG+t	85	8.8	7.8	746	150	135	2.5	4.7	0.6
TG+g+/G-G-g-	86	9.5	7.8	530	366	252	1.9	3.6	3.1
TG-g+/G+G+g+	87	9.4	8.1	628	271	266	1.1	2.3	3.5
TG-g-/G+Tg+	88	8.9	8.2	696	211	182	1.5	1.3	0.9
G+G+g-/G+G+g-	89	8.4	8.2	813	218	192	0.2	1.2	0.1
G+G+t/TG-g-	90	8.3	8.4	594	339	267	0.5	0.0	0.4
TG-g-/G+G-g+	91	10.1	8.4	587	351	261	3.0	2.0	0.1
TG-g-/TTg-	92	8.7	8.4	719	178	154	2.1	0.8	0.5
TG+g+/G-G-g+	93	9.6	8.4	759	213	202	0.1	0.3	1.7
G+G+t/TG+t	94	9.0	8.5	543	348	245	2.1	5.1	0.2
G+G+g-/TG+t	95	9.9	8.5	583	288	251	0.4	3.5	2.7
TG-g-/TTg-	96	9.6	8.5	643	200	183	0.7	0.4	0.8
TG-g-/G+G+g-	97	9.9	8.8	595	337	254	0.2	1.1	1.5
TG+t/TTt	98	8.8	9.0	497	258	187	5.3	4.1	0.5
TG-g-/G-Tg+	99	11.1	9.1	765	196	179	1.9	1.2	0.2
TG-g-/G+G+g-	100	9.6	9.2	964	162	151	4.2	1.6	0.6
G+G+g-/G+G+g-	101	10.5	9.5	728	263	214	0.8	1.4	0.8
G+G+t/TG+t	102	10.1	9.7	553	281	217	0.7	5.1	0.8

^a ΔE and ΔE_0 denote the raw and ZPE corrected relative energies (in kJ mol⁻¹), respectively. and A , B , and C are the rotational constants (in MHz). $|\mu_{g_i}|$ ($g = a, b, c$) are the magnitudes of the electric dipole moment components (in Debye).

^bFor conciseness, we do not add energy ordering ranks to conformers after **XIV**.

Table S2. Theoretical spectroscopic parameters of the sixteen conformers of the TFB dimer calculated at the B3LYP-D3BJ/6-311++G(2d,p) level of theory.^a

Conformers	ΔE	ΔE_0	A	B	C	$ \mu_a $	$ \mu_b $	$ \mu_c $
I(TG-g-/TG+g+)	0.0	0.0	561	304	275	1.1	1.9	1.3
II(TG+g+/TG+g+)	1.9	1.0	538	285	237	0.7	3.4	2.0
III(G-G-g+/TG-g-)	1.0	1.1	605	284	272	0.5	1.3	1.0
IV(TG-g-/TG+t)	2.5	1.2	509	326	260	0.9	5.1	2.0
V(TG+t/TG+t)	3.7	2.0	638	250	198	6.9	3.3	0.2
VI(TG-g-/TG+g+)	3.6	2.4	554	252	204	0.0	2.9	0.5
VII(TG-g-/G-G-t)	2.4	2.6	602	328	266	0.4	2.6	0.2
VIII(TG-g-/G+G+g-)	2.8	2.9	816	200	181	0.1	0.9	0.0
IX(TG-g-/G-G-g+)	2.4	2.6	602	328	266	0.4	2.6	0.2
X(G+G+g-/G-G-t)	2.1	2.3	675	271	267	0.3	0.6	1.2
XI(TG-g-/TG-t)	5.5	4.0	743	200	192	2.5	0.9	1.5
XII(G+G+g-/TG-g-)	3.1	3.4	762	221	208	1.2	1.8	0.8
XIII(TG-g-/TTg-)	3.9	3.2	512	323	239	0.8	3.0	2.0
XIV(G+G+t/TG-g-)	3.8	2.7	563	297	248	0.1	3.1	1.0
XV(TG-g-/G+G+t)	2.9	3.6	814	232	218	0.8	1.2	0.2
XVI(TG-g-/G-G-g+)	5.1	3.9	601	253	205	0.3	0.7	0.3

^a ΔE and ΔE_0 denote the raw and ZPE corrected relative energies (in kJ mol⁻¹), respectively. and A , B , and C are the rotational constants (in MHz). $|\mu_g|$ ($g = a, b, c$) are the magnitudes of the electric dipole moment components (in Debye).

Table S3. Theoretical spectroscopic parameters of the sixteen conformers of the TFB dimer calculated at the B2PLYP-D3BJ/6-311++G(2d,p) level of theory.^a

Conformers	ΔE	ΔE_0	A	B	C	$ \mu_a $	$ \mu_b $	$ \mu_c $
I(TG-g-/TG+g+)	0.0	0.0	561	307	277	1.0	2.0	1.3
II(TG+g+/TG+g+)	1.7	0.8	542	283	237	0.7	3.4	2.1
III(G-G-g+/TG-g-)	1.4	1.2	605	285	272	0.4	1.3	1.0
IV(TG-g-/TG+t)	1.4	0.1	509	330	260	1.0	5.2	2.0
V(TG+t/TG+t)	2.6	1.1	642	249	198	6.9	3.3	0.2
VI(TG-g-/TG+g+)	3.0	1.8	555	253	205	0.0	2.9	0.5
VII(TG-g-/G-G-t)	1.8	2.2	604	331	269	0.4	2.5	0.1
VIII(TG-g-/G+G+g-)	2.7	2.8	819	202	183	0.1	0.9	0.1
IX(TG-g-/G-G-g+)	1.8	2.2	604	332	269	0.4	2.5	0.1
X(G+G+g-/G-G-t)	1.9	1.9	683	271	266	0.4	0.7	1.2
XI(TG-g-/TG-t)	5.1	3.5	760	196	188	2.4	1.1	1.6
XII(G+G+g-/TG-g-)	3.6	3.9	763	218	206	1.2	1.8	0.9
XIII(TG-g-/TTg-)	3.9	3.1	514	325	241	0.7	3.0	2.0
XIV(G+G+t/TG-g-)	3.3	2.2	571	293	246	0.2	3.1	1.0
XV(TG-g-/G+G+t)	3.0	3.6	812	233	220	0.9	1.2	0.2
XVI(TG-g-/G-G-g+)	4.6	3.2	610	252	204	0.3	0.7	0.2

^a ΔE and ΔE_0 denote the raw and ZPE corrected relative energies (in kJ mol⁻¹), respectively. and A , B , and C are the rotational constants (in MHz). $|\mu_g|$ ($g = a, b, c$) are the magnitudes of the electric dipole moment components (in Debye).

Table S4. Theoretical spectroscopic parameters of the sixteen conformers of the TFB dimer calculated at the B2PLYP-D3BJ/def2-TZVP level of theory.^a

Conformers	ΔE	ΔE_0	A	B	C	$ \mu_a $	$ \mu_b $	$ \mu_c $
I(TG-g-/TG+g+)	0.0	0.0	567	298	270	1.1	1.8	1.4
II(TG+g+/TG+g+)	1.7	0.8	543	278	233	0.5	3.4	2.0
III(G-G-g+/TG-g-)	1.9	1.8	609	279	268	0.4	1.3	1.1
IV(TG-g-/TG+t)	2.0	0.7	516	318	256	0.9	5.0	2.1
V(TG+t/TG+t)	2.8	1.2	639	245	195	6.7	3.4	0.2
VI(TG-g-/TG+g+)	2.6	1.6	558	248	201	0.1	2.9	0.4
VII(TG-g-/G-G-t)	2.7	2.5	619	300	263	0.1	2.2	1.1
VIII(TG-g-/G+G+g-)	2.1	2.4	829	198	181	0.0	0.9	0.1
IX(TG-g-/G-G-g+)	2.5	2.8	608	321	261	0.4	2.5	0.1
X(G+G+g-/G-G-t)	2.6	2.8	686	267	262	0.4	0.7	1.3
XI(TG-g-/TG-t)	3.9	2.7	786	190	181	2.3	1.2	1.5
XII(G+G+g-/TG-g-)	3.5	3.6	787	207	195	1.3	1.8	1.0
XIII(TG-g-/TTg-)	4.1	3.3	519	307	231	0.6	3.0	2.0
XIV(G+G+t/TG-g-)	3.9	2.8	576	282	238	0.1	3.2	0.9
XV(TG-g-/G+G+t)	2.9	3.5	821	229	216	0.8	1.3	0.2
XVI(TG-g-/G-G-g+)	3.9	3.0	618	247	201	0.3	0.7	0.2

^a ΔE and ΔE_0 denote the raw and ZPE corrected relative energies (in kJ mol^{-1}), respectively. and A , B , and C are the rotational constants (in MHz). $|\mu_g|$ ($g = a, b, c$) are the magnitudes of the electric dipole moment components (in Debye).

Table S5. Theoretical spectroscopic parameters of the sixteen conformers of the TFB dimer calculated at the MP2/6-311++G(2d,p) level of theory.^a

Conformers	ΔE	ΔE_0	A	B	C	$ \mu_a $	$ \mu_b $	$ \mu_c $
I(TG-g-/TG+g+)	0.0	0.7	560	312	280	1.0	1.9	1.4
II(TG+g+/TG+g+)	1.9	1.9	543	287	239	0.7	3.4	2.1
III(G-G-g+/TG-g-)	2.5	2.9	601	292	276	0.4	1.4	1.0
IV(TG-g-/TG+t)	0.3	0.0	508	339	263	1.2	5.2	2.1
V(TG+t/TG+t)	2.2	1.6	644	252	200	6.9	3.2	0.3
VI(TG-g-/TG+g+)	3.2	2.9	556	258	208	0.2	2.9	0.5
VII(TG-g-/G-G-t)	0.9	2.2	605	341	275	0.5	2.4	0.1
VIII(TG-g-/G+G+g-)	2.6	3.8	819	206	187	0.2	0.9	0.2
IX(TG-g-/G-G-g+)	0.9	2.2	605	341	275	0.5	2.4	0.1
X(G+G+g-/G-G-t)	2.1	2.8	691	277	268	0.6	1.0	1.2
XI(TG-g-/TG-t)	5.2	4.3	698	218	210	2.4	0.6	2.1
XII(G+G+g-/TG-g-)	5.3	6.5	744	228	216	1.0	1.9	0.8
XIII(TG-g-/TTg-)	4.1	4.1	513	334	246	0.6	3.0	2.0
XIV(G+G+t/TG-g-)	3.5	3.2	576	295	248	0.3	3.1	-1.0
XV(TG-g-/G+G+t)	3.3	4.8	811	236	222	1.1	1.3	0.2
XVI(TG-g-/G-G-g+)	4.7	4.3	612	256	207	0.2	0.7	0.3

^a ΔE and ΔE_0 denote the raw and ZPE corrected relative energies (in kJ mol^{-1}), respectively. and A , B , and C are the rotational constants (in MHz). $|\mu_g|$ ($g = a, b, c$) are the magnitudes of the electric dipole moment components (in Debye).

Table S6. Experimental transition frequencies of the observed parent species of conformer **I** of the TFB dimer.

J'	Ka'	Kc'	J''	Ka''	Kc''	$\nu_{\text{obs}}/\text{MHz}$	$\Delta\nu_{\text{obs-calc}}/\text{MHz}$
3	1	2	2	0	2	2043.9537	-0.0001
3	2	2	2	1	1	2492.9617	0.0000
3	2	2	2	1	2	2573.2380	0.0000
3	2	1	2	1	2	2582.5784	-0.0027
3	2	1	2	1	1	2502.3080	0.0033
3	3	1	2	2	0	3102.4381	0.0073
3	3	1	2	2	1	3104.3118	0.0001
3	3	0	2	2	0	3102.5138	0.0001
3	3	0	2	2	1	3104.3880	-0.0065
4	0	4	3	0	3	2219.0200	0.0050
4	0	4	3	1	3	2006.0320	-0.0096
4	1	4	3	0	3	2393.2226	-0.0021
4	1	4	3	1	3	2180.2410	-0.0103
4	1	3	3	0	3	2660.2213	0.0001
4	1	3	3	1	2	2286.7813	0.0000
4	2	3	3	2	2	2235.8317	-0.0002
4	2	3	3	1	2	3011.8905	-0.0084
4	2	3	3	1	3	3172.3655	0.0001
4	2	2	3	1	3	3199.9860	0.0091
4	2	2	3	2	1	2254.1002	-0.0002
4	2	2	3	1	2	3039.5104	0.0000
4	3	2	3	2	1	3657.8154	-0.0032
4	3	2	3	2	2	3667.1617	0.0001
4	3	1	3	2	2	3667.7372	-0.0028
4	3	1	3	2	1	3658.3972	0.0001
4	4	1	3	3	0	4232.8137	0.0004
4	4	0	3	3	0	4232.8165	0.0002
4	4	0	3	3	1	4232.9003	0.0011
5	0	5	4	0	4	2761.4902	-0.0001
5	0	5	4	1	4	2587.2814	0.0008
5	1	5	4	1	4	2722.2967	-0.0001
5	1	5	4	0	4	2896.5130	0.0065
5	1	4	4	2	2	2101.6220	0.0029
5	1	4	4	1	3	2854.3481	0.0000
5	1	4	4	0	4	3295.5545	0.0001
5	2	4	4	2	3	2792.4100	-0.0099
5	2	4	4	1	3	3517.5393	0.0018
5	2	4	4	1	4	3784.5342	0.0002
5	2	3	4	2	2	2827.4897	-0.0001
5	2	3	4	1	3	3580.2189	0.0000
5	2	3	4	1	4	3847.2168	0.0013
5	3	3	4	2	2	4205.9624	-0.0046
5	3	3	4	3	2	2802.2488	0.0001
5	3	3	4	2	3	4233.5786	0.0001
5	3	2	4	3	1	2803.9712	0.0001
5	3	2	4	2	2	4208.2679	0.0001
5	3	2	4	2	3	4235.8761	-0.0032
5	4	2	4	3	2	4792.8725	0.0002
5	4	2	4	3	1	4792.2954	0.0016
5	4	1	4	3	1	4792.3212	0.0002
5	4	1	4	3	2	4792.8970	-0.0025
5	5	1	5	4	2	2561.4449	0.0000

5	5	1	4	4	1	5362.2498	-0.0044
5	5	1	4	4	0	5362.2491	-0.0021
5	5	0	5	4	1	2561.4178	0.0000
5	5	0	4	4	1	5362.2534	-0.0009
6	0	6	5	0	5	3298.3252	-0.0001
6	0	6	5	1	5	3163.3117	0.0025
6	1	6	5	1	5	3262.7276	-0.0001
6	1	6	5	0	5	3397.7477	0.0038
6	1	5	5	2	3	2692.8410	0.0033
6	1	5	5	0	5	3952.7728	0.0002
6	1	5	5	1	4	3418.7085	0.0000
6	1	5	5	2	4	2755.5193	0.0001
6	2	5	5	1	4	4010.6379	-0.0015
6	2	5	5	1	5	4409.6876	0.0003
6	2	5	5	2	4	3347.4500	0.0000
6	2	4	5	1	5	4529.8048	0.0035
6	2	4	5	1	4	4130.7534	0.0000
6	2	4	5	2	3	3404.8826	0.0000
6	3	4	5	2	3	4742.5469	-0.0030
6	3	4	5	2	4	4805.2315	0.0002
6	3	3	5	3	2	3368.6075	0.0000
6	3	3	5	2	3	4749.3856	0.0002
6	3	3	5	2	4	4812.0689	0.0020
6	4	3	5	3	3	5352.9066	0.0002
6	4	3	5	3	2	5350.6054	-0.0002
6	4	2	5	3	3	5353.0468	0.0049
6	4	2	5	3	2	5350.7470	0.0060
6	5	2	6	4	2	2559.6937	0.0002
6	5	2	5	4	2	5922.1122	0.0003
6	5	2	6	4	3	2559.8291	0.0000
6	5	2	5	4	1	5922.0850	0.0003
6	5	1	6	4	2	2559.6944	-0.0003
6	5	1	5	4	2	5922.1133	0.0003
6	5	1	5	5	0	3360.6680	0.0000
6	5	1	6	4	3	2559.8301	-0.0001
6	5	1	5	4	1	5922.0861	0.0003
6	6	1	6	5	2	3130.9617	0.0008
6	6	1	5	5	0	6491.6279	0.0001
6	6	1	6	5	1	3130.9601	0.0003
6	6	1	5	5	1	6491.6280	0.0001
6	6	0	6	5	2	3130.9612	0.0003
6	6	0	6	5	1	3130.9606	0.0008
6	6	0	5	5	1	6491.6269	-0.0010
7	0	7	6	0	6	3831.0133	0.0005
7	0	7	6	1	6	3731.5954	0.0012
7	1	7	6	0	6	3900.9757	-0.0013
7	1	7	6	1	6	3801.5583	-0.0001
7	1	6	6	2	5	3386.8960	0.0070
7	1	6	6	1	5	3978.8199	0.0000
7	1	6	6	0	6	4633.2675	0.0004
7	2	6	6	3	4	2442.8760	0.0076
7	2	6	6	1	5	4492.5760	-0.0046
7	2	6	6	2	5	3900.6497	0.0001
7	2	6	6	1	6	5047.6000	-0.0092
7	2	5	6	1	6	5251.4686	-0.0122

7	2	5	6	3	4	2646.7470	0.0070
7	2	5	6	2	4	3984.4072	0.0000
7	2	5	6	1	5	4696.4522	0.0000
7	3	5	6	3	4	3926.0502	0.0000
7	3	5	6	2	4	5263.7173	-0.0003
7	3	5	6	2	5	5383.8317	0.0001
7	3	4	6	3	3	3936.0358	-0.0001
7	3	4	6	2	4	5280.5389	0.0002
7	3	4	6	2	5	5400.6527	-0.0001
7	4	4	6	4	3	3924.4190	0.0000
7	4	4	6	3	3	5906.4172	0.0002
7	4	4	6	3	4	5913.2529	0.0003
7	4	3	6	3	3	5906.9115	0.0003
7	4	3	6	4	2	3924.7776	0.0000
7	4	3	6	3	4	5913.7470	0.0002
7	5	3	6	4	3	6481.7494	0.0002
7	5	3	7	4	4	2557.3301	-0.0001
7	5	3	7	4	3	2556.8363	0.0002
7	5	3	6	4	2	6481.6138	0.0000
7	5	3	6	5	2	3921.9230	0.0028
7	5	2	6	4	3	6481.7550	-0.0008
7	5	2	7	4	4	2557.3370	0.0002
7	5	2	6	4	2	6481.6205	0.0002
7	5	2	7	4	3	2556.8425	-0.0002
7	5	2	6	5	1	3921.9256	0.0000
7	6	2	7	5	2	3129.5900	0.0003
7	6	2	6	6	1	3920.5557	0.0000
7	6	2	7	5	3	3129.5967	0.0004
7	6	1	6	6	0	3920.5557	0.0000
7	6	1	7	5	2	3129.5902	0.0004
7	6	1	7	5	3	3129.5966	0.0003
7	7	1	7	6	2	3700.4271	-0.0012
7	7	1	7	6	1	3700.4285	0.0002
7	7	0	7	6	1	3700.4271	-0.0012
7	7	0	7	6	2	3700.4286	0.0002
8	0	8	7	1	7	4291.4990	0.0016
8	0	8	7	0	7	4361.4615	-0.0001
8	1	8	7	1	7	4338.9119	-0.0001
8	1	8	7	0	7	4408.8870	0.0108
8	1	7	7	1	6	4533.5713	0.0000
8	1	7	7	0	7	5335.8255	0.0000
8	1	7	7	2	5	3815.9392	0.0002
8	1	7	7	2	6	4019.8130	0.0024
8	2	7	7	1	7	5697.8480	0.0106
8	2	7	7	2	6	4451.7868	0.0001
8	2	7	7	1	6	4965.5480	0.0007
8	2	6	7	3	5	3284.4145	0.0069
8	2	6	7	2	5	4563.7179	0.0000
8	2	6	7	1	6	5281.3501	0.0000
8	3	6	7	3	5	4487.8189	0.0001
8	3	6	7	2	5	5767.1305	0.0014
8	3	6	7	2	6	5971.0008	0.0001
8	3	5	7	3	4	4507.1188	0.0000
8	3	5	7	2	5	5803.2505	0.0002
8	3	5	7	2	6	6007.1252	0.0033

8	4	5	7	4	4	4487.2554	0.0001
8	4	5	7	3	4	6457.6330	-0.0035
8	4	5	7	3	5	6474.4578	0.0002
8	4	4	7	4	3	4488.2320	0.0001
8	4	4	7	3	4	6459.1074	0.0002
8	4	4	7	3	5	6475.9250	-0.0033
8	5	4	8	4	4	2552.3031	0.0002
8	5	4	8	4	5	2553.7738	0.0001
8	5	4	7	5	3	4483.6988	0.0001
8	5	3	8	4	5	2553.8021	0.0001
8	5	3	7	5	2	4483.7206	0.0001
8	5	3	8	4	4	2552.3315	0.0002
8	6	3	7	6	2	4481.6485	0.0000
8	6	3	8	5	4	3127.5461	0.0000
8	6	3	8	5	3	3127.5180	0.0003
8	6	2	8	5	4	3127.5467	0.0003
8	6	2	7	6	1	4481.6487	0.0000
8	6	2	8	5	3	3127.5180	0.0000
8	7	2	8	6	3	3699.2469	0.0020
8	7	2	8	6	2	3699.2448	0.0002
8	7	2	7	7	1	4480.4600	-0.0050
8	7	1	7	7	0	4480.4598	-0.0052
8	7	1	8	6	3	3699.2451	0.0002
8	7	1	8	6	2	3699.2466	0.0020
8	8	1	8	7	2	4269.8630	0.0084
8	8	1	8	7	1	4269.8547	0.0001
8	8	0	8	7	1	4269.8630	0.0084
8	8	0	8	7	2	4269.8547	0.0001
9	0	9	8	1	8	4843.8110	0.0037
9	0	9	8	0	8	4891.2218	0.0000
9	1	9	8	0	8	4922.4017	0.0013
9	1	9	8	1	8	4874.9858	0.0000
9	1	8	8	0	8	6056.3759	0.0002
9	1	8	8	1	7	5082.0119	0.0002
9	1	8	8	2	7	4650.0330	-0.0026
9	1	8	8	2	6	4334.2332	0.0004
9	2	8	8	1	7	5432.6671	0.0031
9	2	8	8	1	8	6359.6050	-0.0083
9	2	8	8	2	7	5000.6882	0.0003
9	2	7	8	1	7	5888.5187	0.0000
9	2	7	8	2	6	5140.7399	0.0001
9	2	7	8	3	6	3937.3253	-0.0032
9	3	7	8	2	6	6252.3495	-0.0072
9	3	7	8	2	7	6568.1595	0.0001
9	3	7	8	3	6	5048.9457	0.0002
9	3	6	8	2	6	6322.0750	-0.0073
9	3	6	8	4	5	3132.0343	0.0022
9	3	6	8	2	7	6637.8850	0.0000
9	3	6	8	3	5	5082.5499	0.0001
9	4	6	8	4	5	5050.7700	0.0002
9	4	5	8	4	4	5053.0799	0.0001
9	5	5	9	4	6	2549.0764	-0.0003
9	5	5	8	5	4	5046.0729	0.0001
9	5	4	8	5	3	5046.1433	0.0001
9	5	4	9	4	5	2545.3939	-0.0008

9	6	4	9	5	5	3124.6211	0.0000
9	6	4	9	5	4	3124.5224	0.0000
9	6	4	8	6	3	5043.1480	0.0001
9	6	3	9	5	5	3124.6225	0.0000
9	6	3	9	5	4	3124.5238	0.0000
9	6	3	8	6	2	5043.1491	0.0001
9	7	3	9	6	4	3697.5411	0.0013
9	7	3	9	6	3	3697.5386	0.0002
9	7	3	8	7	2	5041.4428	0.0000
9	7	2	9	6	3	3697.5397	0.0013
9	7	2	9	6	4	3697.5400	0.0002
9	7	2	8	7	1	5041.4428	0.0000
9	8	2	8	8	1	5040.3869	0.0000
9	8	2	9	7	2	4268.7988	0.0001
9	8	2	9	7	3	4268.7984	-0.0003
9	8	1	9	7	3	4268.7988	0.0001
9	8	1	9	7	2	4268.7975	-0.0012
9	8	1	8	8	0	5040.3869	0.0000
9	9	1	9	8	2	4839.2471	0.0017
9	9	0	9	8	1	4839.2471	0.0017
10	0	10	9	1	8	4256.0146	-0.0009
10	0	10	9	1	9	5389.9916	0.0009
10	0	10	9	0	9	5421.1693	0.0000
10	1	10	9	0	9	5441.1949	0.0045
10	1	10	9	1	9	5410.0119	0.0001
10	1	9	9	2	8	5273.0776	0.0021
10	1	9	9	1	8	5623.7281	0.0004
10	1	9	9	2	7	4817.2214	0.0007
10	2	9	9	2	8	5547.2604	0.0027
10	2	9	9	1	8	5897.8980	-0.0120
10	2	8	9	3	7	4602.3346	-0.0016
10	2	8	9	1	8	6520.4540	-0.0060
10	2	8	9	2	7	5713.9533	0.0003
10	3	8	9	3	7	5608.9701	0.0004
10	3	7	9	2	7	6843.8114	0.0000
10	3	7	9	3	6	5662.4691	0.0002
10	3	7	9	4	6	3743.7315	0.0002
10	4	7	9	4	6	5614.8631	0.0003
10	4	6	9	4	5	5619.7656	0.0002
10	5	6	10	4	7	2543.3300	0.0112
10	5	6	9	5	5	5609.1053	0.0003
10	5	5	9	5	4	5609.3005	0.0003
10	5	5	10	4	6	2534.9298	0.0002
10	6	5	10	5	6	3120.6256	0.0037
10	6	5	9	6	4	5605.1060	0.0003
10	6	4	9	6	3	5605.1102	0.0003
10	6	4	10	5	5	3120.3420	0.0085
10	7	4	10	6	4	3695.1743	0.0002
10	7	4	10	6	5	3695.1794	-0.0003
10	7	3	10	6	5	3695.1800	0.0002
10	7	3	10	6	4	3695.1715	-0.0027
10	7	3	9	7	2	5602.7460	0.0003
10	8	3	9	8	2	5601.2756	0.0003
10	8	3	10	7	3	4267.3284	0.0001
10	8	3	10	7	4	4267.3250	-0.0034

10	8	2	10	7	4	4267.3285	0.0001
10	8	2	10	7	3	4267.3250	-0.0033
10	8	2	9	8	1	5601.2756	0.0003
10	9	2	10	8	3	4838.2855	-0.0016
10	9	1	10	8	2	4838.2855	-0.0016
10	10	0	10	9	1	5408.6022	0.0001
10	10	1	10	9	2	5408.6022	0.0001
11	0	11	10	1	10	5931.6067	0.0022
11	0	11	10	0	10	5951.6265	0.0009
11	1	11	10	0	10	5964.2456	0.0025
11	1	11	10	1	10	5944.2140	-0.0079
11	1	10	10	2	9	5885.0318	0.0018
11	1	10	10	1	9	6159.2090	-0.0033
11	2	10	10	2	9	6091.4832	-0.0078
11	2	10	10	1	9	6365.6735	0.0002
11	2	9	10	3	8	5275.6130	-0.0038
11	2	9	10	2	8	6282.2509	0.0004
11	3	9	10	3	8	6167.4473	0.0013
11	3	8	10	3	7	6246.0800	-0.0021
11	4	8	10	4	7	6179.3445	0.0010
11	4	8	11	3	9	2006.2539	0.0000
11	4	7	10	4	6	6188.8800	0.0089
11	5	7	10	5	6	6172.8442	0.0010
11	5	6	10	5	5	6173.3267	0.0009
11	6	6	10	6	5	6167.5758	0.0010
11	6	6	11	5	7	3115.3528	-0.0006
11	6	6	11	5	6	3114.5770	0.0000
11	6	5	11	5	6	3114.5958	0.0000
11	6	5	11	5	7	3115.3723	0.0000
11	6	5	10	6	4	6167.5890	0.0010
11	7	5	11	6	6	3692.0179	0.0021
11	7	5	10	7	4	6164.4119	0.0009
11	7	5	11	6	5	3691.9972	0.0002
11	7	4	10	7	3	6164.4121	0.0009
11	7	4	11	6	6	3692.0163	0.0002
11	7	4	11	6	5	3692.0062	0.0090
11	8	4	11	7	4	4265.3484	0.0001
11	8	4	11	7	5	4265.3487	0.0002
11	8	3	11	7	4	4265.3480	-0.0003
11	8	3	11	7	5	4265.3486	0.0001
11	9	3	11	8	4	4836.9892	0.0015
11	9	2	11	8	3	4836.9892	0.0015
11	10	2	10	10	1	6160.2541	0.0007
11	10	2	11	9	3	5407.7200	-0.0038
11	10	1	11	9	2	5407.7200	-0.0038
11	10	1	10	10	0	6160.2541	0.0007
12	0	12	11	1	11	6469.9872	-0.0028
12	1	12	11	0	11	6490.4324	-0.0078
12	1	11	11	2	10	6483.4563	-0.0015
12	1	11	11	1	10	6689.9100	-0.0088
12	2	11	11	1	10	6839.9389	0.0000
12	2	11	11	2	10	6633.5000	0.0220
12	2	10	11	3	9	5952.8723	-0.0016
12	2	10	11	2	9	6844.7031	0.0000
12	3	10	11	4	7	4699.5137	0.0007

12	3	9	12	2	11	2105.1116	-0.0005
12	3	9	11	4	8	5027.1980	0.0004
12	5	8	12	4	9	2530.2038	0.0001
12	8	5	12	7	6	4262.7516	-0.0021
12	8	5	12	7	5	4262.7528	0.0001
12	8	4	12	7	5	4262.7502	-0.0025
12	8	4	12	7	6	4262.7538	0.0001
12	9	4	12	8	5	4835.2814	0.0051
12	9	3	12	8	4	4835.2814	0.0051
12	10	3	12	9	4	5406.5523	-0.0052
12	10	2	12	9	3	5406.5523	-0.0052
13	2	11	12	3	10	6629.3576	0.0003
13	4	10	13	3	11	2056.1990	-0.0001
13	4	9	12	5	8	4842.3750	0.0004
13	5	9	13	4	10	2524.4596	0.0000
13	6	8	13	5	9	3100.4095	0.0000
13	6	7	13	5	8	3096.4366	0.0000
13	7	7	13	6	7	3682.4600	0.0000
13	7	7	13	6	8	3682.6111	0.0000
13	7	6	13	6	8	3682.6145	0.0000
13	7	6	13	6	7	3682.4635	0.0000
13	8	6	13	7	6	4259.4241	0.0001
13	8	6	13	7	7	4259.4252	-0.0023
13	8	5	13	7	6	4259.4252	0.0012
13	8	5	13	7	7	4259.4277	0.0001
13	9	5	13	8	6	4833.0700	-0.0052
13	9	4	13	8	5	4833.0700	-0.0052
13	10	4	13	9	5	5405.0499	0.0015
13	10	3	13	9	4	5405.0499	0.0015
14	7	8	14	6	9	3676.0121	0.0000
14	7	8	14	6	8	3675.6385	0.0000
14	7	7	14	6	9	3676.0225	0.0000
14	7	7	14	6	8	3675.6489	0.0000
14	8	7	14	7	8	4255.2398	-0.0022
14	8	6	14	7	7	4255.2296	-0.0022
14	9	6	14	8	7	4830.2996	0.0003
14	9	5	14	8	6	4830.2994	0.0003
14	10	5	14	9	6	5403.1380	0.0010
14	10	4	14	9	5	5403.1380	0.0010
15	5	10	15	4	11	2359.4290	-0.0012
15	8	8	15	7	9	4250.0568	-0.0010
15	8	7	15	7	8	4250.0291	-0.0009
15	9	7	15	8	8	4826.8600	0.0043
15	9	6	15	8	7	4826.8600	0.0050
16	9	8	16	8	9	4822.6418	-0.0015
16	9	7	16	8	8	4822.6399	-0.0015

Table S7. Experimental transition frequencies of the observed parent species of conformer **II** of the TFB dimer.

J'	Ka'	Kc'	J''	Ka''	Kc''	$\nu_{\text{obs}}/\text{MHz}$	$\Delta\nu_{\text{obs-calc}}/\text{MHz}$
3	2	2	2	1	2	2445.3443	0.0077
3	2	2	2	1	1	2313.6408	-0.0001
3	2	1	2	1	1	2337.7162	-0.0002
3	2	1	2	1	2	2469.4256	0.0134
3	3	1	2	2	1	2970.6498	-0.0015
3	3	1	2	2	0	2965.7579	0.0000
3	3	0	2	2	1	2970.9945	-0.0003
3	3	0	2	2	0	2966.0999	-0.0015
4	1	4	3	0	3	2083.0939	0.0040
4	1	3	3	0	3	2519.6774	0.0006
4	1	3	3	1	2	2073.0215	0.0002
4	2	3	3	1	2	2746.2536	0.0027
4	2	3	3	1	3	3009.3000	0.0041
4	2	2	3	1	3	3079.0154	0.0035
4	2	2	3	1	2	2815.9558	-0.0111
4	3	2	3	2	1	3454.4463	0.0022
4	3	2	3	2	2	3478.5232	0.0035
4	3	1	3	2	2	3480.9015	-0.0054
4	3	1	3	2	1	3456.8370	0.0057
4	4	1	4	3	2	2050.9742	-0.0004
4	4	1	3	3	1	4055.9419	0.0050
4	4	1	3	3	0	4055.5946	0.0012
4	4	1	4	3	1	2048.5870	-0.0004
4	4	0	3	3	1	4055.9579	0.0011
4	4	0	3	3	0	4055.6114	-0.0020
4	4	0	4	3	2	2050.9942	-0.0004
4	4	0	4	3	1	2048.6070	-0.0004
5	0	5	4	1	4	2278.8502	0.0008
5	1	5	4	0	4	2499.9002	0.0000
5	1	4	4	0	4	3148.9410	0.0078
5	1	4	4	1	3	2579.7056	0.0002
5	2	4	4	1	4	3594.0905	0.0053
5	2	4	4	1	3	3157.4980	-0.0004
5	2	4	4	2	3	2484.2690	0.0001
5	2	3	4	1	3	3310.6821	-0.0046
5	2	3	4	2	2	2567.7350	-0.0061
5	2	3	4	1	4	3747.2522	-0.0213
5	3	3	4	2	3	3994.8746	-0.0010
5	3	3	4	2	2	3925.1561	-0.0034
5	3	3	4	0	4	5237.3326	-0.0003
5	3	2	4	2	2	3934.5750	0.0011
5	3	2	4	2	3	4004.2885	-0.0015
5	4	2	4	3	2	4556.9867	-0.0013
5	4	2	5	3	3	2048.3332	-0.0004
5	4	2	4	3	1	4554.5943	-0.0064
5	4	1	4	3	1	4554.7783	-0.0014
5	4	1	4	3	2	4557.1635	-0.0034
5	4	1	5	3	3	2048.5121	-0.0004
5	5	1	5	4	1	2636.8905	0.0000
5	5	1	4	4	1	5143.0821	-0.0007
5	5	1	4	4	0	5143.0633	0.0005
5	5	0	4	4	1	5143.0857	0.0019

5	5	0	4	4	0	5143.0629	-0.0009
5	5	0	5	4	2	2637.0704	0.0000
6	0	6	5	1	5	2776.6929	0.0036
6	1	6	5	0	5	2920.1819	0.0006
6	1	5	5	2	3	2346.0152	0.0005
6	1	5	5	0	5	3814.4492	0.0103
6	1	5	5	2	4	2499.2069	0.0039
6	2	5	5	1	4	3550.1040	0.0027
6	2	5	5	1	5	4199.1370	0.0026
6	2	4	5	1	5	4480.6460	0.0074
6	2	4	5	1	4	3831.6110	0.0054
6	2	4	5	2	3	3100.6247	0.0004
6	3	4	5	2	3	4369.9415	-0.0002
6	3	4	5	2	4	4523.1295	-0.0005
6	3	4	5	3	3	3012.5271	0.0038
6	3	3	5	2	4	4550.6669	-0.0010
6	3	3	5	3	2	3030.6530	0.0062
6	3	3	5	2	3	4397.4755	-0.0041
6	4	3	5	3	2	5049.4906	-0.0032
6	4	3	5	3	3	5058.9073	-0.0009
6	4	3	6	3	4	2046.3844	-0.0004
6	4	2	5	3	2	5050.3789	-0.0020
6	4	2	6	3	4	2047.2750	0.0030
6	4	2	5	3	3	5059.7921	-0.0032
6	4	2	6	3	3	2019.7335	-0.0006
6	5	2	5	4	1	5643.3769	0.0079
6	5	2	6	4	3	2632.9733	-0.0001
6	5	2	5	4	2	5643.5500	0.0021
6	5	1	5	4	2	5643.5673	0.0079
6	5	1	5	4	1	5643.3769	-0.0036
6	5	1	6	4	2	2632.0860	-0.0117
6	6	1	5	5	1	6230.3310	-0.0017
6	6	1	5	5	0	6230.3310	-0.0006
6	6	1	6	5	2	3223.8544	0.0003
6	6	1	6	5	1	3223.8448	0.0022
6	6	0	5	5	1	6230.3310	-0.0017
6	6	0	5	5	0	6230.3310	-0.0007
6	6	0	6	5	2	3223.8544	0.0002
6	6	0	6	5	1	3223.8448	0.0021
7	0	7	6	1	6	3260.8634	0.0041
7	1	7	6	0	6	3348.5217	0.0026
7	1	7	6	1	6	3293.4368	-0.0001
7	1	6	6	0	6	4511.4600	0.0003
7	1	6	6	2	4	2807.5104	0.0001
7	1	6	6	1	5	3562.1200	0.0001
7	1	6	6	2	5	3089.0185	0.0039
7	2	6	6	1	6	4823.2424	0.0099
7	2	6	6	1	5	3928.9753	0.0004
7	2	5	6	3	4	2361.4017	0.0015
7	2	5	6	1	5	4385.3263	-0.0010
7	2	5	6	3	3	2333.8630	0.0006
7	2	5	6	2	4	3630.7178	0.0001
7	2	5	6	1	6	5279.5856	0.0007
7	3	5	6	2	4	4784.8521	-0.0015
7	3	5	6	2	5	5066.3650	0.0071

7	3	5	6	3	4	3515.5361	-0.0001
7	3	4	6	3	3	3554.0324	0.0000
7	3	4	6	2	5	5132.4006	0.0087
7	3	4	6	2	4	4850.8883	0.0006
7	4	4	7	3	5	2047.4810	-0.0055
7	4	4	6	4	3	3516.6425	0.0047
7	4	4	6	3	3	5535.4794	-0.0054
7	4	4	6	3	4	5563.0226	-0.0001
7	4	3	6	3	4	5566.2302	-0.0024
7	4	3	6	4	2	3518.9639	0.0033
7	4	3	7	3	5	2050.6961	-0.0003
7	4	3	6	3	3	5538.6987	0.0040
7	5	3	6	4	2	6142.7132	-0.0009
7	5	3	6	4	3	6143.6014	0.0003
7	5	3	7	4	4	2626.9581	-0.0053
7	5	2	6	4	3	6143.6713	0.0015
7	5	2	6	4	2	6142.7829	0.0003
7	6	2	7	5	3	3220.2127	0.0009
7	6	2	6	5	1	6730.8366	0.0085
7	6	1	6	5	2	6730.8565	0.0162
7	6	1	7	5	2	3220.1447	0.0009
7	7	1	7	6	1	3810.5765	0.0010
7	7	1	7	6	2	3810.5772	0.0010
7	7	0	7	6	2	3810.5772	0.0010
7	7	0	7	6	1	3810.5765	0.0010
8	0	8	7	0	7	3766.8917	0.0000
8	0	8	7	1	7	3734.3155	0.0015
8	1	8	7	2	6	2223.0550	-0.0006
8	1	8	7	1	7	3752.8509	-0.0001
8	1	8	7	0	7	3785.4304	0.0017
8	1	7	7	2	5	3210.2695	-0.0015
8	1	7	7	2	6	3666.6255	0.0021
8	1	7	7	0	7	5228.9979	0.0014
8	1	7	7	1	6	4033.4784	0.0001
8	2	7	7	3	4	2258.1101	0.0005
8	2	7	7	1	6	4301.4790	-0.0080
8	2	7	7	1	7	5464.4310	0.0035
8	2	6	7	3	4	2933.4286	0.0013
8	2	6	7	3	5	2999.4630	0.0017
8	2	6	7	1	7	6139.7400	-0.0051
8	2	6	7	1	6	4976.8020	-0.0026
8	2	6	7	2	5	4153.5978	0.0006
8	3	6	7	2	5	5170.6269	-0.0113
8	3	6	7	3	5	4016.5022	0.0000
8	3	6	7	2	6	5626.9927	0.0022
8	3	5	7	4	4	2105.3042	0.0006
8	3	5	7	2	6	5763.2757	-0.0027
8	3	5	7	2	5	5306.9250	-0.0011
8	4	5	7	3	5	6071.5143	0.0031
8	4	5	8	3	6	2055.0085	-0.0005
8	4	5	7	4	4	4024.0247	0.0000
8	4	5	7	3	4	6005.4760	-0.0011
8	4	4	8	3	6	2064.4461	-0.0003
8	4	4	7	3	5	6080.9465	-0.0021
8	4	4	7	3	4	6014.9141	-0.0005

8	4	4	7	4	3	4030.2522	0.0000
8	5	4	8	4	4	2609.6682	-0.0004
8	5	4	7	4	4	6643.1302	-0.0006
8	5	4	7	4	3	6639.9232	0.0023
8	5	4	8	4	5	2619.1000	-0.0061
8	5	3	7	4	3	6640.2188	0.0034
8	5	3	7	4	4	6643.4250	-0.0003
8	5	3	8	4	4	2609.9628	-0.0004
8	6	3	8	5	4	3214.8010	-0.0029
8	6	3	8	5	3	3214.5104	0.0010
8	6	2	8	5	3	3214.5147	0.0006
8	6	2	8	5	4	3214.8060	-0.0026
8	7	2	8	6	2	3807.3500	-0.0048
8	7	2	8	6	3	3807.3599	0.0004
8	7	1	8	6	2	3807.3500	-0.0049
8	7	1	8	6	3	3807.3599	0.0003
8	8	1	8	7	2	4397.2130	-0.0055
8	8	1	8	7	1	4397.2130	-0.0055
8	8	0	8	7	1	4397.2130	-0.0055
8	8	0	8	7	2	4397.2130	-0.0055
9	0	9	8	0	8	4218.9179	-0.0001
9	0	9	8	1	8	4200.3870	0.0061
9	1	9	8	1	8	4210.6292	-0.0001
9	1	9	8	0	8	4229.1689	0.0026
9	1	8	8	1	7	4492.1661	-0.0001
9	1	8	8	2	7	4224.1503	-0.0072
9	1	8	8	0	8	5954.2725	0.0015
9	1	8	8	2	6	3548.8398	-0.0001
9	2	8	8	3	6	2716.2083	0.0003
9	2	8	8	3	5	2579.9205	0.0004
9	2	8	8	1	8	6120.1433	0.0004
9	2	8	8	1	7	4676.5761	0.0009
9	2	8	8	2	7	4408.5666	0.0000
9	2	7	8	1	7	5609.6150	-0.0066
9	2	7	8	2	6	4666.2953	0.0000
9	2	7	8	3	6	3649.2529	-0.0015
9	3	7	8	2	7	6206.6070	-0.0018
9	3	7	8	3	6	4514.2503	0.0000
9	3	7	8	2	6	5531.2870	-0.0042
9	3	7	8	4	4	2449.8047	0.0008
9	3	6	8	2	6	5780.2820	-0.0067
9	3	6	8	4	4	2698.8020	0.0006
9	3	6	8	3	5	4626.9570	-0.0029
9	3	6	8	2	7	6455.5970	-0.0093
9	3	6	8	4	5	2708.2394	0.0006
9	4	6	9	3	7	2073.0219	-0.0005
9	4	6	8	3	6	6587.2726	-0.0001
9	4	6	8	3	5	6450.9788	-0.0060
9	4	6	8	4	5	4532.2638	0.0001
9	4	5	9	3	7	2096.8415	-0.0005
9	4	5	8	3	5	6474.8029	-0.0014
9	4	5	8	4	4	4546.6459	0.0001
9	4	5	8	3	6	6611.0900	-0.0022
9	5	5	9	4	5	2586.2578	-0.0005
9	5	5	9	4	6	2610.0774	-0.0004

9	5	4	9	4	5	2587.2860	0.0100
9	5	4	9	4	6	2611.0990	0.0034
9	6	4	9	5	4	3206.2029	0.0005
9	6	4	9	5	5	3207.2246	0.0045
9	6	4	8	6	3	4515.6516	0.0000
9	6	3	9	5	4	3206.2285	0.0029
9	6	3	8	6	2	4515.6701	0.0000
9	6	3	9	5	5	3207.2438	0.0005
9	7	3	8	7	2	4511.0512	0.0000
9	7	3	9	6	4	3802.7581	-0.0010
9	7	2	9	6	3	3802.7373	0.0011
9	7	2	8	7	1	4511.0515	0.0000
9	8	2	9	7	3	4394.3004	0.0015
9	8	2	9	7	2	4394.3001	0.0015
9	8	1	9	7	3	4394.3004	0.0015
9	8	1	9	7	2	4394.3001	0.0015
9	9	1	9	8	2	4983.7975	0.0000
9	9	0	9	8	1	4983.7975	0.0000
10	0	10	9	1	9	4661.7605	0.0010
10	0	10	9	0	9	4672.0160	0.0082
10	0	10	9	1	8	2936.6540	-0.0007
10	1	10	9	0	9	4677.5480	-0.0023
10	1	10	9	1	9	4667.3020	-0.0001
10	1	9	9	2	8	4757.8176	-0.0040
10	1	9	9	2	7	3824.7750	-0.0002
10	1	9	9	0	9	6677.5837	0.0000
10	1	9	10	0	10	2005.5781	0.0022
10	2	9	9	1	9	6787.4709	0.0013
10	2	9	9	1	8	5062.3603	-0.0046
10	2	9	9	2	8	4877.9500	-0.0058
10	2	9	10	1	10	2120.1692	0.0016
10	2	8	9	1	8	6283.8864	0.0016
10	2	8	9	2	7	5166.4294	0.0000
10	3	8	9	3	7	5007.7736	0.0000
10	3	8	9	4	5	2910.9320	0.0003
10	3	8	9	2	8	6805.8166	0.0006
10	3	8	9	2	7	5872.7746	0.0051
10	3	7	9	2	7	6283.6797	0.0004
10	3	7	9	4	6	3345.6550	-0.0060
10	4	7	9	3	6	6864.5945	-0.0009
10	4	7	10	3	8	2105.8187	-0.0005
10	4	7	10	1	10	6153.8483	0.0014
10	4	6	9	5	4	2482.7331	0.0005
10	4	6	9	3	6	6917.8528	-0.0002
10	4	6	9	5	5	2483.7508	0.0005
10	4	6	10	3	8	2159.0730	-0.0039
10	5	6	10	4	7	2601.4000	0.0041
10	5	5	10	4	6	2551.1300	-0.0075
10	6	5	10	5	5	3194.1373	-0.0003
10	6	5	10	5	6	3197.1499	0.0131
10	6	4	10	5	6	3197.2284	-0.0003
10	6	4	10	5	5	3194.2263	-0.0032
10	7	4	10	6	4	3796.3347	0.0006
10	7	4	10	6	5	3796.4266	0.0006
10	7	3	10	6	4	3796.3364	0.0006

10	7	3	10	6	5	3796.4282	0.0006
10	8	3	10	7	3	4390.2717	0.0013
10	8	3	10	7	4	4390.2734	0.0013
10	8	2	10	7	3	4390.2718	0.0013
10	8	2	10	7	4	4390.2734	0.0013
10	9	2	10	8	3	4981.0923	0.0000
10	9	1	10	8	2	4981.0923	0.0000
10	9	1	10	8	3	4981.0923	0.0000
11	0	11	10	0	10	5125.8681	0.0000
11	0	11	10	1	10	5120.3314	0.0059
11	1	11	10	1	10	5123.2717	0.0000
11	1	11	10	0	10	5128.8196	0.0054
11	1	10	11	0	11	2268.4486	0.0028
11	1	10	10	2	9	5268.5899	-0.0138
11	1	10	10	1	9	5388.7378	-0.0001
11	2	10	10	2	9	5343.3523	0.0000
11	2	10	10	1	9	5463.4817	-0.0049
11	2	10	11	1	11	2340.2507	0.0024
11	2	9	10	2	8	5651.9560	-0.0059
11	2	9	10	3	7	4534.7120	0.0000
11	3	9	11	2	10	2080.8280	-0.0072
11	3	9	10	2	8	6202.6660	-0.0015
11	3	9	10	4	6	3337.2508	0.0003
11	4	8	11	3	9	2157.3872	-0.0005
11	5	7	11	4	8	2595.5490	0.0035
11	6	6	11	5	7	3184.4479	-0.0002
11	6	6	11	5	6	3176.6405	-0.0006
11	6	5	11	5	7	3184.7564	-0.0002
11	6	5	11	5	6	3176.9526	0.0030
11	7	5	11	6	6	3787.9834	0.0004
11	7	4	11	6	6	3787.9907	0.0004
11	7	4	11	6	5	3787.6823	0.0004
11	8	4	11	7	5	4384.8842	0.0011
11	8	3	11	7	4	4384.8770	0.0011
11	9	3	11	8	4	4977.4710	0.0000
11	9	2	11	8	3	4977.4709	0.0000
11	10	2	11	9	3	5567.7794	0.0000
11	10	1	11	9	2	5567.7794	0.0000
12	0	12	11	1	11	5577.2728	0.0023
12	1	12	11	0	11	5581.7573	-0.0037
12	1	11	11	1	10	5835.3945	-0.0002
12	1	11	11	2	10	5760.6460	-0.0001
12	2	11	11	1	10	5880.2258	-0.0018
12	2	11	12	1	12	2566.9080	-0.0044
12	2	11	11	2	10	5805.4789	-0.0001
12	2	10	11	3	8	4947.9855	-0.0002
12	3	10	11	2	9	6530.1917	-0.0018
12	4	9	12	3	10	2230.9320	-0.0066
12	5	8	12	4	9	2595.9350	0.0027
12	6	7	12	5	8	3169.4530	0.0078
12	6	6	12	5	8	3170.3545	-0.0009
12	9	4	12	8	5	4972.7437	0.0000
12	9	3	12	8	4	4972.7431	0.0000
12	10	3	12	9	4	5564.4593	0.0000
12	10	2	12	9	3	5564.4593	0.0000

13	0	13	12	0	12	6034.8490	-0.0031
13	0	13	12	1	12	6033.3033	-0.0045
13	1	13	12	1	12	6034.1000	-0.0080
13	1	13	12	0	12	6035.6507	-0.0017
13	1	12	12	2	11	6238.9823	0.0000
13	2	12	13	1	13	2797.9070	-0.0029
13	2	12	12	1	11	6309.9422	0.0038
13	2	11	12	3	9	5287.1614	-0.0017
13	3	11	12	2	10	6865.3920	0.0073
13	7	6	13	6	7	3760.9640	0.0074
13	9	5	13	8	6	4966.6991	0.0000
13	9	4	13	8	5	4966.6970	0.0000
13	10	4	13	9	5	5560.2142	-0.0001
13	10	3	13	9	4	5560.2141	-0.0001
14	0	14	13	1	13	6488.8482	0.0016
14	1	14	13	0	13	6490.0555	-0.0020
14	1	13	13	2	12	6708.0655	0.0000
14	1	13	14	0	14	3017.1250	-0.0038
14	2	13	13	1	12	6749.0633	0.0000
14	3	12	13	4	10	4601.1177	-0.0002
14	10	5	14	9	6	5554.8829	-0.0001
14	10	4	14	9	5	5554.8828	-0.0001
15	0	15	14	1	14	6944.1127	-0.0014
15	1	15	14	2	13	3912.7304	0.0000
15	1	15	14	0	14	6944.7324	-0.0014
15	5	11	15	4	12	2676.1250	-0.0045
15	6	9	14	7	8	3841.7523	0.0010
19	7	12	18	8	11	5349.4725	0.0092

Table S8. Experimental transition frequencies of the observed parent species of conformer **IV** of the TFB dimer.

J'	Ka'	Kc'	J''	Ka''	Kc''	$\nu_{\text{obs}}/\text{MHz}$	$\Delta\nu_{\text{obs-calc}}/\text{MHz}$
3	2	2	2	1	1	2299.9459	0.0000
3	2	2	2	1	2	2487.0596	-0.0002
3	2	1	2	1	2	2545.8056	-0.0003
3	2	1	2	1	1	2358.6919	-0.0001
3	3	1	2	2	1	2867.8212	-0.0001
3	3	1	2	2	0	2855.4956	0.0000
3	3	0	2	2	0	2857.0541	-0.0001
3	3	0	2	2	1	2869.3798	-0.0001
4	0	4	3	1	3	2056.5365	-0.0005
4	0	4	3	0	3	2154.7300	0.0000
4	1	4	3	0	3	2209.6006	-0.0072
4	1	3	3	0	3	2822.6388	-0.0002
4	2	3	3	1	2	2769.5420	0.0002
4	2	3	3	2	2	2247.1437	0.0000
4	2	3	3	1	3	3142.2045	-0.0002
4	2	2	3	1	2	2930.2088	-0.0005
4	2	2	3	1	3	3302.8721	-0.0001
4	3	2	3	3	1	2277.4985	0.0000
4	3	2	3	2	1	3393.9474	0.0004
4	3	2	3	2	2	3452.6960	0.0029
4	3	1	3	2	1	3404.6040	-0.0001
4	3	1	3	2	2	3463.3509	0.0007

4	4	1	3	3	0	3893.2509	0.0030
4	4	0	3	3	1	3894.9722	0.0030
4	4	0	3	3	0	3893.4200	0.0093
5	0	5	4	1	4	2597.1808	-0.0006
5	0	5	4	0	4	2652.0591	0.0000
5	1	5	4	0	4	2679.5766	0.0001
5	1	4	4	2	3	2488.7635	-0.0005
5	1	4	4	1	3	2906.5224	-0.0002
5	1	4	4	0	4	3574.4420	0.0104
5	1	4	4	2	2	2328.0990	0.0026
5	2	4	4	2	3	2793.7140	-0.0003
5	2	4	4	1	4	3824.5027	-0.0015
5	2	4	4	1	3	3211.4733	0.0003
5	2	3	4	1	4	4152.8278	0.0002
5	2	3	4	1	3	3539.7962	-0.0001
5	3	3	4	2	2	3894.5380	0.0019
5	3	3	4	2	3	4055.2028	-0.0008
5	3	2	4	2	3	4095.8414	0.0019
5	3	2	4	2	2	3935.1717	-0.0002
5	4	2	4	3	2	4465.6292	-0.0005
5	4	2	4	3	1	4454.9704	-0.0021
5	4	1	4	3	2	4467.0740	0.0015
5	4	1	4	3	1	4456.4150	-0.0004
5	5	1	4	4	1	4925.7084	-0.0001
5	5	1	4	4	0	4925.5492	0.0035
5	5	0	4	4	0	4925.5610	-0.0001
5	5	0	4	4	1	4925.7250	0.0011
6	0	6	5	1	5	3120.3995	-0.0003
6	1	6	5	0	5	3160.7313	0.0001
6	1	6	5	1	5	3133.2330	0.0191
6	1	5	5	2	4	3131.0240	-0.0020
6	1	5	5	0	5	4358.3512	0.0023
6	1	5	5	2	3	2802.7000	-0.0027
6	1	5	5	1	4	3435.9763	-0.0002
6	2	5	5	1	5	4530.9878	-0.0023
6	2	5	5	1	4	3636.1353	0.0003
6	2	5	5	2	4	3331.1843	-0.0003
6	2	4	5	2	3	3562.8540	0.0052
6	2	4	5	1	4	4196.1256	0.0031
6	2	4	5	1	5	5090.9779	0.0002
6	3	4	5	2	3	4351.9197	0.0004
6	3	4	5	2	4	4680.2428	0.0001
6	3	3	5	2	3	4463.7994	-0.0002
6	3	3	5	3	2	3490.0000	0.0022
6	3	3	5	2	4	4792.1249	0.0019
6	4	3	5	3	3	5041.3810	0.0061
6	4	3	5	3	2	5000.7392	0.0001
6	4	2	5	3	3	5048.3961	0.0001
6	4	2	5	3	2	5007.7601	0.0000
6	5	2	6	4	3	2068.5204	0.0008
6	5	2	5	4	1	5492.4738	-0.0024
6	5	2	5	4	2	5493.9189	-0.0003
6	5	1	5	4	1	5492.6429	-0.0003
6	5	1	5	4	2	5494.0821	-0.0039
6	6	1	6	5	1	2540.4006	0.0004

6	6	1	5	5	1	5957.0989	-0.0004
6	6	1	6	5	2	2540.5675	0.0004
6	6	1	5	5	0	5957.0787	-0.0053
6	6	0	6	5	1	2540.4019	0.0004
6	6	0	5	5	1	5957.0981	-0.0026
6	6	0	6	5	2	2540.5688	0.0004
6	6	0	5	5	0	5957.0849	-0.0004
7	0	7	6	1	6	3632.8934	0.0021
7	0	7	6	0	6	3645.7027	-0.0026
7	1	7	6	1	6	3638.5675	0.0000
7	1	7	6	0	6	3651.3834	0.0019
7	1	6	6	1	5	3941.5089	0.0000
7	1	6	6	0	6	5151.9373	-0.0033
7	1	6	6	2	5	3741.3528	0.0024
7	2	6	6	3	3	2398.4010	0.0131
7	2	6	6	1	5	4059.4851	0.0003
7	2	6	6	1	6	5257.1026	0.0001
7	2	6	6	2	5	3859.3263	0.0000
7	2	5	6	1	5	4905.4712	-0.0013
7	2	5	6	2	4	4145.3265	0.0001
7	2	5	6	3	4	3356.2430	-0.0130
7	2	5	6	1	6	6103.0904	0.0001
7	2	5	6	3	3	3244.3754	-0.0002
7	3	5	6	2	4	4770.8121	-0.0036
7	3	5	6	2	5	5330.8033	0.0001
7	3	5	6	3	4	3981.7452	0.0000
7	3	4	6	2	4	5015.4260	0.0001
7	3	4	6	2	5	5575.4135	0.0001
7	4	4	6	4	3	4004.2417	0.0001
7	4	4	6	3	4	5626.8631	-0.0002
7	4	4	6	3	3	5514.9803	-0.0027
7	4	3	6	3	4	5651.4717	0.0005
7	4	3	6	4	2	4021.8287	0.0001
7	4	3	6	3	3	5539.5910	0.0001
7	5	3	6	4	2	6055.1368	0.0005
7	5	3	6	5	2	3993.6378	0.0001
7	5	3	6	4	3	6062.1524	-0.0049
7	5	3	7	4	4	2057.9165	0.0008
7	5	2	6	5	1	3994.4530	0.0001
7	5	2	6	4	3	6063.1400	0.0006
7	5	2	7	4	3	2034.2906	0.0007
7	5	2	6	4	2	6056.1188	0.0003
7	6	2	6	5	1	6524.9375	0.0003
7	6	2	6	5	2	6525.1043	0.0002
7	6	2	7	5	2	2530.4845	0.0002
7	6	2	7	5	3	2531.4666	0.0003
7	6	1	7	5	2	2530.5020	0.0002
7	6	1	7	5	3	2531.4841	0.0003
7	6	1	6	5	2	6525.1219	0.0003
7	6	1	6	5	1	6524.9549	0.0002
7	7	1	6	6	1	6988.5151	-0.0002
7	7	1	6	6	0	6988.5138	-0.0002
7	7	1	7	6	2	3003.9791	0.0007
7	7	0	6	6	0	6988.5139	-0.0002
7	7	0	7	6	1	3003.9617	0.0007

7	7	0	6	6	1	6988.5152	-0.0002
8	0	8	7	0	7	4145.3346	-0.0001
8	0	8	7	1	7	4139.6590	0.0006
8	1	8	7	1	7	4142.0857	0.0000
8	1	8	7	0	7	4147.7647	0.0027
8	1	7	7	1	6	4433.5362	-0.0002
8	1	7	7	0	7	5939.7719	0.0001
8	1	7	7	2	6	4315.5627	0.0021
8	2	7	7	1	6	4496.9478	-0.0002
8	2	7	7	1	7	5997.5072	0.0001
8	2	7	7	2	6	4378.9717	-0.0004
8	2	7	7	3	4	2662.8810	-0.0040
8	2	6	7	3	4	3832.7790	-0.0036
8	2	6	7	1	6	5666.8457	0.0001
8	2	6	7	3	5	4077.3943	0.0015
8	2	6	7	2	5	4702.8821	0.0001
8	3	6	7	3	5	4536.1210	0.0000
8	3	6	7	2	6	6007.5980	0.0001
8	3	6	7	2	5	5161.6120	0.0018
8	3	6	7	4	3	2866.3945	-0.0004
8	3	5	7	3	4	4740.3186	0.0002
8	3	5	7	4	4	3339.8124	0.0019
8	3	5	7	2	5	5610.4183	0.0004
8	3	5	7	2	6	6456.4056	0.0000
8	4	5	7	3	5	6227.8647	0.0001
8	4	5	7	3	4	5983.2552	0.0008
8	4	5	7	4	4	4582.7461	-0.0003
8	4	5	7	5	2	2523.8483	-0.0004
8	4	4	7	3	4	6051.9290	-0.0207
8	4	4	8	1	7	3452.4754	-0.0009
8	4	4	7	4	3	4626.8338	-0.0001
8	4	4	7	3	5	6296.5612	0.0013
8	4	4	7	5	3	2593.5258	-0.0003
8	5	4	7	5	3	4573.8214	0.0000
8	5	4	7	4	3	6607.1299	0.0009
8	5	4	7	4	4	6631.7370	0.0000
8	5	4	8	4	5	2048.9915	0.0009
8	5	3	7	5	2	4576.9713	-0.0002
8	5	3	7	4	4	6635.8704	0.0011
8	5	3	7	4	3	6611.2615	0.0001
8	5	3	8	4	5	2053.1238	0.0010
8	6	3	7	6	2	4560.8883	0.0000
8	6	3	8	5	4	2518.5334	0.0001
8	6	2	8	5	3	2514.5216	0.0001
8	6	2	7	6	1	4560.9913	0.0000
8	7	2	8	6	3	2995.7103	0.0007
8	7	1	8	6	2	2995.5915	0.0007
8	8	1	8	7	1	3467.2887	0.0005
8	8	1	8	7	2	3467.2903	0.0004
8	8	0	8	7	1	3467.2886	0.0004
8	8	0	8	7	2	3467.2904	0.0005
9	0	9	8	1	8	4643.6368	0.0026
9	0	9	8	0	8	4646.0614	-0.0001
9	1	9	8	1	8	4644.6458	0.0003
9	1	9	8	0	8	4647.0768	0.0040

9	1	8	9	0	9	2071.7940	0.0004
9	1	8	8	2	7	4860.0090	0.0026
9	2	8	8	1	8	6747.2077	0.0000
9	2	8	8	2	7	4891.7863	0.0000
9	2	8	9	1	9	2102.5592	-0.0030
9	2	8	8	1	7	4955.1960	-0.0018
9	2	7	8	3	6	4772.8036	0.0047
9	2	7	8	2	6	5231.5272	0.0001
9	2	7	9	1	9	3612.1965	-0.0042
9	2	7	8	1	7	6464.8363	0.0000
9	2	7	8	3	5	4323.9911	-0.0002
9	3	7	8	2	6	5539.0547	-0.0075
9	3	7	8	2	7	6708.9599	0.0000
9	3	7	8	4	4	3319.8948	-0.0003
9	3	6	8	4	5	4110.0014	0.0083
9	3	6	8	2	6	6260.4650	0.0001
9	3	6	8	4	4	4041.2981	0.0003
9	4	6	8	3	6	6849.7495	0.0000
9	4	6	8	4	5	5158.0061	0.0001
9	4	6	8	5	3	3104.8828	-0.0003
9	4	6	8	3	5	6400.9425	0.0006
9	4	5	9	1	8	3778.3270	-0.0033
9	4	5	8	3	6	7009.7108	0.0000
9	4	5	8	4	4	5249.2724	0.0005
9	4	5	8	5	4	3268.9768	0.0001
9	4	5	8	3	5	6560.9052	0.0020
9	5	5	8	5	4	5156.6815	0.0001
9	5	5	9	4	6	2047.6671	0.0012
9	5	4	8	5	3	5166.3987	0.0001
9	5	4	8	6	2	2651.8768	-0.0002
9	5	4	8	6	3	2651.9973	-0.0002
9	6	4	8	6	3	5140.0816	0.0001
9	6	4	9	5	5	2501.9334	0.0000
9	6	3	9	5	5	2502.5226	0.0000
9	6	3	8	6	2	5140.5503	0.0001
9	6	3	9	5	4	2488.6730	-0.0001
9	7	3	9	6	4	2983.9480	0.0007
9	7	2	9	6	3	2983.3723	0.0007
9	8	2	9	7	3	3459.7388	-0.0016
9	8	2	9	7	2	3459.7274	0.0005
9	8	1	9	7	2	3459.7255	-0.0016
9	8	1	9	7	3	3459.7410	0.0005
9	9	1	9	8	2	3930.5087	0.0014
9	9	1	9	8	1	3930.5073	0.0002
9	9	0	9	8	2	3930.5075	0.0002
9	9	0	9	8	1	3930.5086	0.0014
10	0	10	9	1	9	5146.3300	-0.0009
10	0	10	9	0	9	5147.3422	0.0001
10	1	10	9	1	9	5146.7439	0.0001
10	1	10	9	0	9	5147.7557	0.0007
10	1	9	9	2	8	5384.6195	0.0038
10	1	9	9	1	8	5416.3948	-0.0007
10	1	9	10	0	10	2340.8500	0.0030
10	2	9	9	1	8	5431.5280	-0.0021
10	2	9	10	1	10	2355.5710	0.0023

10	2	9	9	2	8	5399.7502	0.0000
10	2	8	9	3	7	5426.1160	0.0012
10	2	8	9	2	7	5733.6499	0.0000
10	3	8	9	3	7	5614.0012	0.0001
10	3	8	9	4	5	3684.6239	-0.0003
10	3	8	10	2	9	2031.4246	0.0001
10	3	8	9	2	7	5921.5356	-0.0007
10	3	7	9	4	5	4734.5139	0.0003
10	3	7	9	3	6	5942.4878	0.0001
10	3	7	9	4	6	4894.4752	0.0004
10	3	7	9	2	7	6971.4150	-0.0105
10	4	7	9	4	6	5726.8969	0.0001
10	4	7	9	3	6	6774.9097	0.0000
10	4	7	9	5	4	3665.3780	-0.0034
10	4	6	9	4	5	5885.5706	0.0000
10	4	6	9	5	5	3997.8665	0.0005
10	4	6	10	1	9	4247.5062	0.0009
10	4	6	9	5	4	3984.0170	0.0004
10	5	6	9	5	5	5741.0181	0.0001
10	5	6	9	6	3	3238.4980	0.0026
10	5	6	9	6	4	3239.0846	0.0000
10	5	6	10	4	7	2061.7888	0.0017
10	5	5	10	2	8	4171.0086	0.0001
10	5	5	9	6	4	3278.1085	0.0001
10	6	5	9	6	4	5722.3408	0.0001
10	6	5	10	5	6	2483.2520	-0.0041
10	6	4	10	5	5	2446.5167	-0.0003
10	6	4	9	6	3	5724.0363	0.0001
10	7	4	10	6	5	2968.0123	0.0006
10	7	3	10	6	4	2965.8026	0.0005
10	8	3	10	7	3	3449.2385	0.0000
10	8	3	10	7	4	3449.3136	0.0000
10	8	2	10	7	3	3449.2399	0.0000
10	8	2	10	7	4	3449.3150	0.0000
10	9	2	10	8	3	3923.4880	-0.0027
10	9	2	10	8	2	3923.4895	0.0002
10	9	1	10	8	2	3923.4870	-0.0023
10	9	1	10	8	3	3923.4909	0.0002
10	10	1	10	9	1	4393.6547	0.0001
10	10	1	10	9	2	4393.6547	0.0001
10	10	0	10	9	2	4393.6547	0.0001
10	10	0	10	9	1	4393.6547	0.0001
11	0	11	10	1	10	5648.4670	0.0005
11	0	11	10	0	10	5648.8796	0.0003
11	1	11	10	1	10	5648.6327	0.0003
11	1	11	10	0	10	5649.0493	0.0041
11	1	10	11	0	11	2604.8137	-0.0018
11	1	10	10	1	9	5912.8350	-0.0128
11	1	10	10	2	9	5897.7126	-0.0007
11	1	10	10	2	8	4054.1747	-0.0005
11	2	10	10	1	9	5919.7864	-0.0006
11	2	10	11	1	11	2611.5930	0.0042
11	2	10	10	2	9	5904.6526	0.0001
11	2	9	11	1	10	2165.9933	0.0029
11	2	9	10	3	8	6032.2792	0.0000

11	2	9	10	2	8	6220.1657	0.0001
11	2	9	10	3	7	4982.3950	0.0050
11	3	9	10	4	7	4255.5878	-0.0003
11	3	9	10	2	8	6325.7846	-0.0011
11	3	9	11	2	10	2264.6713	0.0000
11	3	9	10	4	6	3936.9524	-0.0005
11	3	9	11	0	11	4876.4264	0.0004
11	3	9	10	3	8	6137.8995	0.0001
11	3	8	10	3	7	6502.9704	0.0000
11	3	8	10	4	7	5670.5360	-0.0123
11	4	8	11	3	9	2031.1568	0.0030
11	4	8	10	5	5	4185.9309	-0.0001
11	4	7	10	5	6	4779.6810	-0.0050
11	5	7	11	4	8	2099.7500	-0.0052
11	5	7	10	6	4	3839.1696	0.0005
11	5	7	10	5	6	6324.7101	0.0001
11	5	6	10	5	5	6380.7999	0.0002
11	5	6	10	6	5	3936.5680	0.0007
11	6	6	10	7	3	3339.5366	0.0002
11	6	6	11	5	7	2466.1691	-0.0002
11	6	5	11	5	6	2378.5009	-0.0007
11	6	5	10	7	4	3347.0550	-0.0023
11	7	5	11	6	5	2940.1096	-0.0004
11	7	5	11	6	6	2947.5562	0.0005
11	7	4	11	6	5	2940.4397	-0.0001
11	8	4	11	7	5	3435.3440	-0.0001
11	8	4	10	8	3	6273.1978	0.0001
11	8	4	11	7	4	3435.0141	-0.0001
11	8	3	11	7	5	3435.3528	-0.0001
11	8	3	11	7	4	3435.0229	-0.0001
11	8	3	10	8	2	6273.2052	0.0001
11	9	3	10	9	2	6263.7936	0.0001
11	9	3	11	8	4	3914.0833	-0.0032
11	9	2	11	8	3	3914.0770	-0.0008
11	9	2	10	9	1	6263.7937	0.0001
11	10	2	11	9	3	4387.0396	0.0001
11	10	2	11	9	2	4387.0394	0.0001
11	10	1	11	9	3	4387.0396	0.0001
11	10	1	11	9	2	4387.0394	0.0001
11	11	1	11	10	1	4856.7510	0.0042
11	11	0	11	10	2	4856.7510	0.0041
12	0	12	11	0	11	6150.5286	0.0002
12	0	12	11	1	11	6150.3638	0.0012
12	1	12	11	1	11	6150.4285	0.0002
12	1	12	11	0	11	6150.5954	0.0012
12	1	11	11	2	10	6404.7262	-0.0005
12	1	11	12	0	12	2865.9522	-0.0008
12	2	11	11	1	10	6414.7552	-0.0005
12	2	10	12	1	11	2458.0907	0.0001
12	2	10	11	3	9	6598.1459	0.0000
12	3	10	11	2	9	6759.3268	-0.0012
12	3	10	12	2	11	2510.5625	-0.0002
12	3	9	11	4	8	6414.9920	-0.0052
12	4	9	12	3	10	2213.2537	0.0028
12	4	9	11	5	6	4640.9361	-0.0003

12	4	8	11	5	7	5600.2760	-0.0099
12	5	8	11	6	5	4431.2799	0.0001
12	5	8	12	4	9	2168.8526	0.0076
12	5	7	11	6	6	4642.0995	0.0005
12	6	7	12	5	8	2456.6646	-0.0003
12	6	7	11	7	4	3947.5075	0.0027
12	6	6	12	5	7	2274.3836	-0.0052
12	6	6	11	7	5	3968.9270	-0.0050
12	7	6	12	6	7	2923.0248	0.0004
12	7	5	12	6	6	2903.1399	-0.0007
12	8	5	12	7	6	3417.1504	-0.0005
12	8	4	12	7	5	3415.9857	0.0052
12	10	3	12	9	3	4378.3962	0.0001
12	10	3	12	9	4	4378.3972	0.0001
12	10	2	12	9	4	4378.3972	0.0001
12	10	2	12	9	3	4378.3962	0.0001
12	11	2	12	10	2	4850.4450	-0.0006
12	11	1	12	10	3	4850.4450	-0.0006
12	12	1	12	11	2	5319.7926	0.0002
12	12	0	12	11	1	5319.7926	0.0002
13	0	13	12	1	12	6652.1583	0.0018
13	0	13	12	0	12	6652.2226	0.0003
13	1	13	12	1	12	6652.1826	0.0003
13	1	13	12	0	12	6652.2498	0.0018
13	1	12	12	2	11	6908.7384	-0.0003
13	1	12	13	0	13	3125.5650	0.0057
13	2	12	12	1	11	6913.1722	-0.0003
13	2	12	13	1	13	3126.8773	-0.0002
13	2	11	13	1	12	2737.5592	0.0003
13	3	11	13	2	12	2764.0097	0.0001
13	3	10	12	4	8	6245.1263	0.0001
13	3	10	13	2	11	2186.8790	0.0007
13	4	10	13	3	11	2423.2696	0.0013
13	4	9	12	5	8	6437.0949	0.0138
13	5	9	13	4	10	2273.7570	0.0001
13	5	9	12	6	7	5021.8000	0.0060
13	6	8	12	7	5	4560.1339	0.0003
13	6	8	13	5	9	2462.5775	-0.0001
13	6	7	12	7	6	4614.3761	0.0004
13	6	7	13	5	8	2131.1180	0.0015
13	7	7	13	6	8	2896.2657	-0.0008
13	7	6	13	6	7	2847.1210	0.0031
13	7	6	12	8	5	4044.3429	0.0002
13	8	6	13	7	7	3394.1715	0.0016
13	8	5	13	7	6	3390.4661	-0.0007
13	9	5	13	8	6	3885.9634	-0.0001
13	9	4	13	8	5	3885.7919	-0.0001
13	10	4	13	9	4	4367.3198	0.0000
13	10	4	13	9	5	4367.3250	0.0000
13	10	3	13	9	4	4367.3199	0.0000
13	10	3	13	9	5	4367.3251	0.0000
13	11	3	13	10	3	4842.3829	-0.0043
13	11	2	13	10	4	4842.3830	-0.0043
13	12	2	13	11	3	5313.7451	0.0001
13	12	1	13	11	2	5313.7451	0.0001

13	13	1	13	12	2	5782.7959	0.0000
13	13	0	13	12	1	5782.7959	0.0000
14	1	13	14	0	14	3384.3260	0.0024
14	2	13	14	1	14	3384.8870	-0.0001
14	2	12	14	1	13	3008.6608	-0.0001
14	3	12	14	2	13	3021.4676	-0.0002
14	3	11	13	4	9	6514.7431	0.0000
14	4	11	13	5	8	5242.3888	-0.0002
14	4	11	14	3	12	2654.5233	0.0016
14	5	10	14	4	11	2415.7710	-0.0039
14	6	9	14	5	10	2492.3733	0.0003
14	7	8	13	8	5	4652.9494	0.0003
14	7	8	14	6	9	2871.1125	-0.0010
14	7	7	13	8	6	4664.1572	0.0004
14	8	7	14	7	8	3366.2290	0.0083
14	8	6	14	7	7	3355.8128	-0.0038
14	9	6	14	8	7	3866.0223	-0.0001
14	9	5	14	8	6	3865.4190	-0.0001
14	10	5	14	9	6	4353.3668	0.0000
14	10	5	14	9	5	4353.3432	0.0000
14	10	4	14	9	5	4353.3438	0.0000
14	10	4	14	9	6	4353.3674	0.0000
14	11	4	14	10	4	4832.2524	-0.0019
14	11	3	14	10	5	4832.2531	-0.0019
14	12	3	14	11	3	5306.1499	0.0001
14	12	3	14	11	4	5306.1499	0.0001
14	12	2	14	11	4	5306.1499	0.0001
14	12	2	14	11	3	5306.1499	0.0001
14	13	2	14	12	3	5776.9596	0.0000
14	13	1	14	12	2	5776.9596	0.0000
15	1	14	15	0	15	3642.5992	-0.0002
15	2	14	15	1	15	3642.8362	-0.0002
15	2	13	15	1	14	3274.7445	0.0003
15	3	13	15	2	14	3280.7531	0.0003
15	3	12	15	2	13	2822.8969	0.0015
15	4	12	15	3	13	2900.3588	0.0008
15	6	10	15	5	11	2553.5592	0.0011
15	7	9	15	6	10	2853.6029	-0.0011
15	7	9	14	8	6	5272.4435	0.0007
15	7	8	14	8	7	5301.3895	0.0008
15	8	8	15	7	9	3333.9410	-0.0011
15	8	7	15	7	8	3307.5978	-0.0013
15	9	7	15	8	8	3841.3256	-0.0002
15	9	6	15	8	7	3839.4414	-0.0002
15	10	6	15	9	7	4336.0067	0.0000
15	10	5	15	9	6	4335.9178	0.0000
15	11	5	15	10	5	4819.6930	0.0038
15	11	4	15	10	6	4819.6930	0.0008
15	12	4	15	11	4	5296.7506	0.0001
15	12	4	15	11	5	5296.7507	0.0001
15	12	3	15	11	5	5296.7507	0.0001
15	12	3	15	11	4	5296.7506	0.0001
15	13	3	15	12	4	5769.7420	0.0000
15	13	2	15	12	3	5769.7420	0.0000
15	14	2	15	13	3	6240.1031	0.0000

15	14	1	15	13	2	6240.1031	0.0000
16	2	14	16	1	15	3537.9230	0.0112
16	3	14	16	2	15	3540.6460	-0.0141
16	3	13	16	2	14	3114.5781	0.0012
16	5	12	16	4	13	2799.4510	-0.0059
16	6	11	16	5	12	2651.2206	0.0019
16	7	10	16	6	11	2851.5677	-0.0011
16	8	9	16	7	10	3299.3553	-0.0014
16	8	8	16	7	9	3238.7410	-0.0025
16	9	8	16	8	9	3811.3998	-0.0002
16	9	7	16	8	8	3806.0920	0.0058
16	10	7	16	9	8	4314.6713	-0.0001
16	10	6	16	9	7	4314.3666	-0.0001
16	11	6	16	10	6	4804.2833	-0.0013
16	11	5	16	10	7	4804.2962	-0.0013
16	12	5	16	11	6	5285.2629	0.0000
16	12	5	16	11	5	5285.2626	0.0000
16	12	4	16	11	5	5285.2626	0.0000
16	12	4	16	11	6	5285.2629	0.0000
16	13	4	16	12	5	5760.9318	0.0000
16	13	3	16	12	4	5760.9317	0.0000
16	14	3	16	13	4	6233.2009	0.0000
16	14	2	16	13	3	6233.2009	0.0000
17	2	15	17	1	16	3799.3649	0.0002
17	3	15	17	2	16	3800.5957	0.0002
17	7	11	17	6	12	2873.5277	-0.0008
17	9	9	17	8	10	3776.1871	-0.0005
17	9	8	17	8	9	3762.4984	-0.0006
17	10	8	17	9	9	4288.7520	-0.0001
17	10	7	17	9	8	4287.8097	-0.0001
17	12	6	17	11	6	5271.3678	0.0000
17	12	6	17	11	7	5271.3694	0.0000
17	12	5	17	11	7	5271.3695	0.0000
17	12	5	17	11	6	5271.3679	0.0000
17	13	5	17	12	6	5750.2966	0.0000
17	13	4	17	12	5	5750.2966	0.0000
18	1	17	18	0	18	4415.9258	-0.0005
18	2	17	18	1	18	4415.9422	-0.0005
18	7	12	18	6	13	2927.1828	-0.0001
18	8	11	18	7	12	3241.1410	0.0031
18	10	8	18	9	9	4255.0059	-0.0002
19	2	17	19	1	18	4319.4691	-0.0001
19	3	17	19	2	18	4319.7037	-0.0001
19	6	14	19	5	15	3163.3117	0.0021
19	9	11	19	8	12	3694.3740	0.0048
20	2	18	20	1	19	4578.6864	-0.0003
20	3	18	20	2	19	4578.7867	-0.0003
20	8	13	20	7	14	3245.7512	-0.0011

Table S9. Experimental transition frequencies of the observed parent species of conformer **V** of the TFB dimer.

J'	Ka'	Kc'	J''	Ka''	Kc''	$\nu_{\text{obs}}/\text{MHz}$	$\Delta\nu_{\text{obs-cal}}/\text{MHz}$
2	2	1	1	1	0	2097.4863	0.0000
2	2	0	1	1	1	2151.5647	0.0000
3	2	2	2	1	1	2483.1742	0.0000
3	2	1	2	1	2	2654.0224	0.0000
3	3	1	2	2	0	3390.2822	-0.0066
3	3	0	2	2	1	3394.9500	-0.0070
4	0	4	3	0	3	1699.1366	-0.0002
4	1	4	3	0	3	1921.3874	0.0000
4	1	4	3	1	3	1633.9247	0.0003
4	1	3	3	1	2	1831.0715	-0.0019
4	2	3	3	2	2	1737.9374	-0.0010
4	2	3	3	1	2	2843.4826	0.0000
4	3	2	3	2	1	3816.3210	-0.0003
4	3	2	4	2	3	2100.2595	0.0000
4	3	1	3	2	2	3839.9207	0.0003
4	4	1	4	3	2	2913.0474	0.0000
4	4	1	3	3	0	4662.3309	0.0008
4	4	0	3	3	1	4662.5895	0.0008
4	4	0	4	7	1	2911.3364	0.0000
5	0	5	4	1	4	1874.9748	0.0000
5	0	5	4	0	4	2097.2256	0.0003
5	1	5	4	0	4	2257.9051	0.0000
5	1	5	4	1	4	2035.6550	0.0005
5	1	4	4	1	3	2278.8220	-0.0018
5	2	4	4	2	3	2166.9025	-0.0010
5	2	4	4	1	3	3179.3127	0.0000
5	2	3	4	2	2	2246.3055	-0.0021
5	2	3	4	1	4	3817.6726	0.0002
5	3	3	5	2	4	2122.8446	0.0000
5	3	3	4	3	2	2189.4873	-0.0013
5	3	3	4	2	2	4225.6364	0.0005
5	3	2	4	3	1	2194.5935	-0.0015
5	3	2	4	2	3	4296.5775	0.0005
5	4	2	5	3	3	2910.0934	0.0000
5	4	2	4	4	1	2186.5333	-0.0013
5	4	2	4	3	1	5097.8684	0.0089
5	4	1	5	3	2	2903.3672	0.0000
5	4	1	4	4	0	2186.6246	-0.0013
5	4	1	4	3	2	5099.6937	0.0089
5	5	1	4	4	0	5932.1768	0.0011
5	5	0	4	4	1	5932.1888	0.0011
6	0	6	5	1	5	2324.6354	0.0000
6	0	6	5	0	5	2485.3157	0.0007
6	1	6	5	1	5	2434.0070	0.0007
6	1	6	5	0	5	2594.6860	0.0000
6	1	5	5	1	4	2718.5900	0.0012
6	2	5	5	2	4	2592.2683	-0.0010
6	2	5	5	1	4	3492.7583	0.0002
6	2	4	5	2	3	2718.5960	-0.0012
6	2	4	5	1	5	4500.6154	0.0002
6	3	4	6	2	5	2160.6180	0.0000
6	3	4	5	2	3	4609.3642	-0.0068

6	3	4	5	3	3	2630.0455	0.0028
6	3	3	5	3	2	2643.3793	-0.0017
6	3	3	5	2	4	4773.0511	-0.0034
6	4	3	6	3	4	2907.0012	0.0000
6	4	3	5	4	2	2626.9491	-0.0014
6	4	3	5	3	2	5530.2247	0.0097
6	4	2	5	3	3	5537.5627	0.0075
6	4	2	5	4	1	2627.3575	-0.0015
6	4	2	6	3	3	2887.3452	0.0000
6	5	2	5	5	1	2623.1341	-0.0014
6	5	2	5	4	1	6368.6863	0.0009
6	5	1	5	4	2	6368.7943	0.0009
6	5	1	5	5	0	2623.1389	-0.0014
7	0	7	6	1	6	2758.3750	0.0000
7	0	7	6	0	6	2867.7468	0.0009
7	1	7	6	1	6	2829.2016	0.0008
7	1	7	6	0	6	2938.5718	0.0000
7	1	6	6	1	5	3147.7790	0.0001
7	2	6	6	2	5	3013.4627	0.0053
7	2	6	6	1	5	3787.6269	0.0002
7	2	5	6	1	6	5258.3476	0.0004
7	2	5	6	2	4	3191.7376	-0.0007
7	3	5	7	2	6	2217.5771	0.0000
7	3	5	6	3	4	3070.4143	-0.0021
7	3	5	6	2	4	4961.1878	-0.0024
7	3	4	6	2	5	5280.1631	-0.0060
7	3	4	6	3	3	3099.3811	-0.0027
7	4	4	6	4	3	3068.8726	0.0049
7	4	4	7	3	5	2905.4524	0.0000
7	4	4	6	3	3	5955.7029	0.0013
7	4	3	7	3	4	2858.1769	0.0000
7	4	3	6	3	4	5977.7291	0.0012
7	4	3	6	4	2	3070.2136	-0.0019
7	5	3	6	5	2	3063.1065	-0.0015
7	5	3	6	4	2	6804.4372	0.0028
7	5	2	6	4	3	6804.9800	0.0028
7	5	2	6	5	1	3063.1327	-0.0015
7	6	2	6	6	1	3059.7821	-0.0042
7	6	1	6	6	0	3059.7821	-0.0044
8	0	8	7	0	7	3248.3929	-0.0028
8	0	8	7	1	7	3177.5698	0.0000
8	1	8	7	1	7	3221.6789	-0.0025
8	1	8	7	0	7	3292.5073	0.0000
8	1	7	7	2	6	2924.1994	0.0000
8	1	7	7	1	6	3564.0453	-0.0020
8	2	7	8	1	8	2189.3720	0.0000
8	2	7	7	2	6	3430.0316	-0.0007
8	2	7	7	1	6	4069.8760	-0.0041
8	2	6	7	2	5	3660.6746	-0.0018
8	3	6	7	3	5	3509.6164	-0.0017
8	3	6	7	2	5	5279.0625	-0.0075
8	3	5	7	2	6	5831.0690	-0.0048
8	3	5	7	3	4	3564.3605	-0.0016
8	4	5	8	3	6	2908.1078	0.0000
8	4	5	7	4	4	3512.2718	-0.0016

8	4	5	7	3	4	6368.5924	0.0011
8	4	4	7	3	5	6423.2346	0.0010
8	4	4	7	4	3	3515.9241	0.0020
8	5	4	7	5	3	3504.3541	-0.0014
8	5	3	7	5	2	3504.4582	-0.0014
8	6	3	7	6	2	3499.4123	-0.0014
8	6	2	7	6	1	3499.4138	-0.0014
8	7	2	7	7	1	3496.4728	-0.0014
8	7	1	7	7	0	3496.4729	-0.0014
9	0	9	8	1	8	3585.3312	0.0000
9	0	9	8	0	8	3629.4416	-0.0013
9	1	9	8	0	8	3656.1089	0.0000
9	1	9	8	1	8	3612.0007	0.0033
9	1	8	8	1	7	3966.3278	-0.0001
9	1	8	8	2	7	3460.4949	-0.0001
9	2	8	9	1	9	2419.1317	0.0000
9	2	8	8	2	7	3841.7571	0.0000
9	2	8	8	1	7	4347.5902	0.0003
9	2	7	8	2	6	4121.7503	0.0015
9	3	7	9	2	8	2401.9732	0.0000
9	3	7	8	2	6	5564.9528	-0.0082
9	3	7	8	3	6	3946.5686	0.0013
9	3	6	8	2	7	6439.7959	0.0008
9	3	6	8	3	5	4038.7536	0.0001
9	4	6	8	4	5	3956.9540	-0.0009
9	4	6	9	3	7	2918.4953	0.0000
9	4	6	8	3	5	6761.1852	0.0011
9	4	5	9	3	6	2736.4917	0.0000
9	4	5	8	4	4	3965.5080	-0.0004
9	4	5	8	3	6	6879.1250	0.0012
9	5	5	8	5	4	3947.0350	0.0001
9	5	4	8	5	3	3947.3702	0.0001
9	6	4	8	6	3	3940.0530	0.0004
9	6	3	8	6	2	3940.0598	0.0004
9	7	3	8	7	2	3935.8631	0.0005
9	7	2	8	7	1	3935.8631	0.0005
9	8	2	8	8	1	3933.1700	-0.0084
9	8	1	8	8	0	3933.1700	-0.0084
10	0	10	9	0	9	4011.6111	0.0016
10	0	10	9	1	9	3984.9434	0.0000
10	1	10	9	0	9	4027.3600	-0.0035
10	1	10	9	1	9	4000.6976	0.0001
10	1	9	9	2	8	3974.6521	-0.0002
10	1	9	9	1	8	4355.9161	0.0018
10	2	9	9	2	8	4248.6351	0.0002
10	2	9	10	1	10	2667.0691	0.0000
10	2	9	9	1	8	4629.8972	0.0003
10	2	8	9	3	7	3129.1644	0.0000
10	2	8	9	2	7	4572.3779	0.0013
10	3	8	10	2	9	2533.5588	0.0000
10	3	8	9	2	7	5823.4259	-0.0067
10	3	8	9	3	7	4380.2240	0.0036
10	3	7	9	3	6	4520.5633	0.0009
10	4	7	10	3	8	2940.7316	0.0000
10	4	7	9	4	6	4402.4584	0.0017

10	4	6	9	4	5	4420.3710	0.0017
10	5	6	9	5	5	4391.2677	0.0028
10	5	5	9	5	4	4392.1936	0.0027
10	6	5	9	6	4	4381.8330	-0.0008
10	6	4	9	6	3	4381.8608	0.0017
10	7	4	9	7	3	4376.0793	0.0022
10	7	3	9	7	2	4376.0797	0.0022
10	8	3	9	8	2	4372.3928	0.0009
10	8	2	9	8	1	4372.3928	0.0009
10	9	2	9	9	1	4369.8871	0.0003
10	9	1	9	9	0	4369.8871	0.0003
11	0	11	10	1	10	4379.1183	0.0000
11	0	11	10	0	10	4394.8758	0.0034
11	1	11	10	1	10	4388.2621	0.0027
11	1	11	10	0	10	4404.0134	0.0000
11	1	10	10	2	9	4462.5312	-0.0002
11	1	10	11	0	11	2750.4821	0.0000
11	1	10	10	1	9	4736.5209	0.0069
11	2	10	11	1	11	2929.7296	0.0000
11	2	10	10	1	9	4924.9026	0.0002
11	2	10	10	2	9	4650.9249	0.0051
11	2	9	10	2	8	5010.4133	0.0069
11	2	9	10	3	8	3759.3520	0.0016
11	3	9	11	2	10	2692.3100	0.0000
11	3	9	10	3	8	4809.6740	0.0030
11	3	9	10	2	8	6060.7248	-0.0022
11	3	8	10	3	7	5005.2541	-0.0009
11	4	8	11	3	9	2979.1329	0.0000
11	4	8	10	4	7	4848.0745	0.0022
11	4	7	11	3	8	2513.2478	0.0000
11	4	7	10	4	6	4882.2051	0.0008
11	5	7	10	5	6	4837.0938	-0.0022
11	5	6	10	5	5	4839.3680	-0.0007
11	6	6	10	6	5	4824.8891	0.0015
11	6	5	10	6	4	4824.9694	0.0015
11	7	5	10	7	4	4817.2157	0.0015
11	7	4	10	7	3	4817.2174	0.0015
11	8	4	10	8	3	4812.3003	-0.0008
11	8	3	10	8	2	4812.3003	-0.0009
11	9	3	10	9	2	4808.9723	0.0069
11	9	2	10	9	1	4808.9723	0.0069
11	10	2	10	10	1	4806.5947	0.0027
11	10	1	10	10	0	4806.5947	0.0027
12	0	12	11	0	11	4778.9731	0.0018
12	0	12	11	1	11	4769.8369	0.0066
12	1	12	11	0	11	4784.1989	0.0000
12	1	12	11	1	11	4775.0610	0.0031
12	1	11	11	1	10	5112.7880	0.0022
12	1	11	12	0	12	3084.2967	0.0000
12	1	11	11	2	10	4924.3971	-0.0003
12	2	11	11	2	10	5049.0868	-0.0002
12	2	11	11	1	10	5237.4746	-0.0008
12	2	10	11	3	9	4383.6079	-0.0004
12	2	10	11	2	9	5433.9260	-0.0029
12	2	10	12	1	11	2151.5208	0.0000

12	3	10	11	3	9	5234.2217	0.0009
12	3	10	11	2	9	6284.5424	0.0010
12	3	9	11	3	8	5487.1563	0.0025
12	4	9	12	3	10	3037.7897	0.0000
12	4	9	11	4	8	5292.8759	-0.0017
12	4	8	11	4	7	5352.6771	-0.0024
12	5	8	11	5	7	5284.4681	-0.0022
12	5	7	11	5	6	5289.5388	0.0006
12	6	7	11	6	6	5269.3375	-0.0019
12	6	6	11	6	5	5269.5656	0.0016
12	7	6	11	7	5	5259.3744	0.0019
12	7	5	11	7	4	5259.3803	0.0019
12	8	5	11	8	4	5252.9735	-0.0049
12	8	4	11	8	3	5252.9735	-0.0050
12	9	4	11	9	3	5248.6395	-0.0036
12	9	3	11	9	2	5248.6395	-0.0036
12	10	3	11	10	2	5245.5618	0.0002
12	10	2	11	10	1	5245.5618	0.0002
12	11	1	11	11	0	5243.2889	0.0000
12	11	2	11	11	1	5243.2889	0.0000
13	0	13	12	0	12	5163.6344	-0.0039
13	0	13	12	1	12	5158.4087	-0.0020
13	1	13	12	0	12	5166.5925	0.0000
13	1	13	12	1	12	5161.3622	-0.0027
13	1	12	13	0	13	3409.1378	0.0001
13	1	12	12	1	11	5488.4781	-0.0012
13	2	12	12	1	11	5568.4505	-0.0028
13	2	12	12	2	11	5443.7609	-0.0028
13	2	12	13	1	13	3486.1577	0.0002
13	2	11	12	3	10	4991.1777	-0.0001
13	2	11	12	2	10	5841.7939	0.0035
13	3	11	12	2	10	6504.0377	0.0010
13	3	11	12	3	10	5653.4260	0.0018
13	3	11	13	2	12	3087.1042	0.0000
13	3	10	12	4	9	3708.3521	-0.0002
13	3	10	12	3	9	5961.2192	0.0010
13	4	10	12	4	9	5735.8038	-0.0047
13	4	10	13	3	11	3120.1741	0.0000
13	4	9	12	4	8	5832.6668	-0.0018
13	4	9	13	3	10	2250.2239	0.0000
13	5	9	12	5	8	5733.1767	0.0008
13	5	8	12	5	7	5743.5924	-0.0067
13	6	8	12	6	7	5715.3005	0.0006
13	6	7	12	6	6	5715.8687	0.0005
13	7	7	12	7	6	5702.6497	-0.0039
13	7	6	12	7	5	5702.6674	-0.0049
13	8	6	12	8	5	5694.4988	0.0009
13	8	5	12	8	4	5694.4992	0.0009
13	9	5	12	9	4	5688.9771	0.0008
13	9	4	12	9	3	5688.9771	0.0008
13	10	4	12	10	3	5685.0569	0.0007
13	10	3	12	10	2	5685.0570	0.0008
13	11	3	12	11	2	5682.1678	0.0005
13	11	2	12	11	1	5682.1678	0.0005
13	12	2	12	12	1	5679.9742	0.0004

13	12	1	12	12	0	5679.9742	0.0004
14	0	14	13	0	13	5548.6674	0.0006
14	0	14	13	1	13	5545.7092	-0.0034
14	1	14	13	1	13	5547.3662	0.0007
14	1	14	13	0	13	5550.3189	-0.0008
14	1	13	13	1	12	5865.6106	0.0003
14	1	13	13	2	12	5785.6360	-0.0003
14	2	13	14	1	14	3774.4335	0.0001
14	2	13	13	1	12	5915.6156	0.0001
14	2	13	13	2	12	5835.6409	-0.0006
14	2	12	13	3	11	5572.3003	-0.0008
14	2	12	13	2	11	6234.5518	0.0044
14	3	12	13	3	11	6067.1143	0.0008
14	3	12	14	2	13	3318.5763	0.0000
14	3	11	13	3	10	6423.8059	0.0025
14	4	11	13	4	10	6175.7654	0.0009
14	4	10	13	4	9	6321.1977	-0.0017
14	4	10	14	3	11	2147.6198	0.0000
14	5	10	13	5	9	6182.8068	0.0002
14	5	9	13	5	8	6202.7769	-0.0009
14	6	9	13	6	8	6162.8497	0.0000
14	6	8	13	6	7	6164.1723	-0.0001
14	7	8	13	7	7	6147.1616	0.0001
14	7	7	13	7	6	6147.2144	0.0001
14	8	7	13	8	6	6136.9362	0.0001
14	8	6	13	8	5	6136.9376	0.0001
14	9	6	13	9	5	6130.0228	0.0002
14	9	5	13	9	4	6130.0228	0.0002
14	10	5	13	10	4	6125.1211	0.0003
14	10	4	13	10	3	6125.1211	0.0003
14	11	4	13	11	3	6121.5122	0.0004
14	11	3	13	11	2	6121.5122	0.0004
14	12	3	13	12	2	6118.7739	0.0004
14	12	2	13	12	1	6118.7739	0.0004
15	0	15	14	1	14	5932.2613	-0.0012
15	0	15	14	0	14	5933.9149	-0.0005
15	1	15	14	0	14	5934.8313	-0.0012
15	1	15	14	1	14	5933.1790	-0.0005
15	1	14	14	1	13	6244.7677	-0.0005
15	1	14	14	2	13	6194.7631	0.0001
15	1	14	15	0	15	4036.9338	0.0000
15	2	14	14	2	13	6225.3899	-0.0011
15	2	14	14	1	13	6275.3961	0.0000
15	2	14	15	1	15	4066.6448	0.0000
15	2	13	15	1	14	3244.1065	0.0000
15	2	13	14	3	12	6120.2938	0.0005
15	2	13	14	2	12	6615.1103	0.0047
15	3	13	14	3	12	6475.4025	0.0008
15	3	13	15	2	14	3568.5872	0.0003
15	3	12	15	2	13	2201.4753	0.0000
15	3	12	14	4	11	5092.9432	-0.0002
15	3	12	14	3	11	6872.3650	0.0042
15	4	12	15	3	13	3365.1399	0.0000
15	4	12	14	4	11	6611.7179	0.0014
15	4	11	14	4	10	6814.7681	-0.0010

15	5	11	14	5	10	6632.7383	0.0006
15	5	10	14	5	9	6668.6117	-0.0012
15	6	10	14	6	9	6612.0145	0.0002
15	6	9	14	6	8	6614.8799	-0.0001
15	7	9	14	7	8	6593.0013	0.0002
15	7	8	14	7	7	6593.1378	0.0002
15	8	8	14	8	7	6580.3724	0.0003
15	8	7	14	8	6	6580.3766	0.0003
15	9	7	14	9	6	6571.8409	0.0004
15	9	6	14	9	5	6571.8410	0.0004
15	10	6	14	10	5	6565.8017	0.0004
15	10	5	14	10	4	6565.8017	0.0004
15	12	4	14	12	3	6557.9921	0.0006
15	12	3	14	12	2	6557.9921	0.0006
16	0	16	15	0	15	6319.2924	-0.0009
16	0	16	15	1	15	6318.3749	-0.0014
16	1	16	15	1	15	6318.8805	-0.0009
16	1	16	15	0	15	6319.7970	-0.0014
16	1	15	15	2	14	6595.1581	0.0008
16	1	15	15	1	14	6625.7838	-0.0014
16	2	15	15	1	14	6644.2290	0.0000
16	2	15	15	2	14	6613.5993	-0.0017
16	2	15	16	1	16	4361.3645	0.0001
16	2	14	15	2	13	6988.1670	0.0045
16	3	14	15	3	13	6878.6593	0.0007
16	3	13	15	4	12	5786.1890	-0.0008
16	4	13	16	3	14	3529.2816	0.0003
16	4	13	15	4	12	7042.8019	0.0020
16	8	9	15	8	8	7024.8890	0.0005
16	8	8	15	8	7	7024.9011	0.0004
16	9	8	15	9	7	7014.4915	0.0005
16	9	7	15	9	6	7014.4918	0.0005
16	10	7	15	10	6	7007.1447	0.0006
16	10	6	15	10	5	7007.1447	0.0006
16	12	5	15	12	4	6997.6592	0.0007
16	12	4	15	12	3	6997.6592	0.0007
17	0	17	16	0	16	6704.7427	-0.0014
17	0	17	16	1	16	6704.2374	-0.0016
17	1	17	16	1	16	6704.5140	-0.0014
17	1	17	16	0	16	6705.0189	-0.0016
17	1	16	16	1	15	7008.2389	-0.0023
17	2	16	17	1	17	4657.6000	0.0034
17	2	16	16	2	15	7000.7450	-0.0026
17	3	15	17	2	16	4110.3502	-0.0061
17	5	13	17	4	14	3814.0407	0.0004
17	6	12	17	5	13	4433.5583	0.0002
18	1	17	18	0	18	4948.4061	0.0000
18	2	17	18	1	18	4954.6760	-0.0028
18	2	16	18	1	17	4294.8297	0.0007
18	7	12	18	6	13	5257.1198	-0.0020
18	7	11	18	6	12	5217.3776	-0.0039
19	3	17	19	2	18	4687.0380	0.0006
19	7	13	19	6	14	5227.0799	-0.0007
20	2	18	20	1	19	4941.7511	-0.0043

Table S10. Experimental transition frequencies of the observed parent species of conformer **XIII** of the TFB dimer.

J'	Ka'	Kc'	J''	Ka''	Kc''	$\nu_{\text{obs}}/\text{MHz}$	$\Delta\nu_{\text{obs-calc}}/\text{MHz}$
3	3	1	2	2	0	2849.6907	-0.0001
3	3	0	2	2	1	2869.0800	-0.0050
4	2	3	3	1	3	3113.8985	0.0000
4	2	3	3	1	2	2660.7693	-0.0002
4	2	2	3	1	3	3328.3091	0.0004
4	3	2	3	2	2	3428.8512	0.0000
4	3	2	3	2	1	3349.0025	0.0024
4	3	1	3	2	2	3445.3929	-0.0160
4	3	1	3	2	1	3365.5577	0.0000
4	4	1	3	3	1	3896.6357	-0.0034
4	4	1	3	3	0	3894.2011	0.0006
4	4	0	3	3	1	3896.9245	-0.0040
4	4	0	3	3	0	3894.4900	0.0000
5	0	5	4	1	4	2405.9130	-0.0005
5	1	5	4	0	4	2476.7594	-0.0004
5	1	4	4	0	4	3553.3753	0.0000
5	2	4	4	1	3	3047.7053	-0.0078
5	2	4	4	1	4	3790.4189	0.0000
5	2	3	4	1	3	3477.3893	0.0000
5	3	3	4	2	3	4013.9692	0.0032
5	3	3	4	2	2	3799.5523	-0.0035
5	3	2	4	2	3	4076.1850	0.0002
5	3	2	4	2	2	3861.7747	0.0000
5	4	2	4	3	2	4440.6937	0.0074
5	4	2	4	3	1	4424.1290	0.0003
5	4	1	4	3	1	4426.6830	0.0006
5	4	1	4	3	2	4443.2430	0.0029
5	5	1	4	4	0	4931.4240	-0.0057
5	5	1	4	4	1	4931.7192	0.0000
5	5	0	4	4	1	4931.7550	0.0048
5	5	0	4	4	0	4931.4608	0.0000
6	0	6	5	1	5	2883.7034	-0.0004
6	1	6	5	0	5	2915.8579	-0.0043
6	1	5	5	0	5	4342.7742	-0.0001
6	1	5	5	2	4	2958.2758	0.0070
6	2	5	5	1	4	3417.8389	0.0051
6	2	5	5	1	5	4494.4550	0.0058
6	2	4	5	1	4	4137.7103	-0.0001
6	3	4	5	2	4	4627.5672	-0.0003
6	3	4	5	2	3	4197.8911	-0.0002
6	3	3	5	2	4	4794.6887	0.0078
6	3	3	5	2	3	4365.0048	0.0000
6	4	3	5	3	3	4992.3106	-0.0001
6	4	3	5	3	2	4930.0887	-0.0031
6	4	2	5	3	3	5004.6394	0.0050
6	4	2	5	3	2	4942.4220	0.0064
6	5	2	5	4	2	5471.8209	-0.0039

6	5	2	5	4	1	5469.2708	-0.0003
6	5	1	5	4	1	5469.6049	-0.0020
6	5	1	5	4	2	5472.1613	0.0006
6	6	1	5	5	0	5967.4964	-0.0083
6	6	1	5	5	1	5967.5358	0.0001
6	6	0	5	5	0	5967.5079	0.0001
6	6	0	5	5	1	5967.5329	-0.0060
7	0	7	6	1	6	3351.0422	0.0047
7	1	7	6	0	6	3364.7201	0.0052
7	1	6	6	2	5	3524.0827	-0.0008
7	1	6	6	0	6	5134.8283	-0.0007
7	2	6	6	1	5	3792.7172	0.0032
7	2	6	6	1	6	5219.6255	-0.0006
7	2	5	6	1	5	4862.0055	-0.0003
7	2	5	6	3	3	3025.5938	0.0000
7	3	5	6	2	4	4552.5700	-0.0064
7	3	5	6	2	5	5272.4528	-0.0002
7	3	4	6	2	4	4906.2290	-0.0049
7	3	4	6	2	5	5626.1108	0.0003
7	4	4	6	3	3	5391.0948	0.0000
7	4	4	6	3	4	5558.2085	0.0002
7	4	3	6	3	4	5600.7753	-0.0048
7	4	3	6	3	3	5433.6671	0.0004
7	5	3	6	4	3	6012.4903	0.0002
7	5	3	6	4	2	6000.1658	-0.0005
7	5	2	6	4	2	6002.1319	0.0002
7	5	2	6	4	3	6014.4526	-0.0029
7	6	2	6	5	2	6507.2081	0.0000
7	6	2	6	5	1	6506.8684	-0.0038
7	6	1	6	5	1	6506.9122	0.0000
7	6	1	6	5	2	6507.2531	0.0050
8	0	8	7	1	7	3813.2532	0.0016
8	1	8	7	0	7	3818.8181	0.0017
8	1	7	7	0	7	5916.4042	0.0028
8	1	7	7	2	6	4047.8121	-0.0006
8	2	7	7	1	6	4189.0148	0.0000
8	2	6	7	1	6	5642.0842	-0.0025
8	2	6	7	3	5	3893.7205	0.0033
8	3	6	7	2	6	5948.2423	0.0001
8	3	6	7	2	5	4878.9553	0.0049
8	3	5	7	2	5	5506.1433	0.0014
8	4	5	7	3	4	5792.0344	-0.0009
8	4	5	7	3	5	6145.6882	-0.0046
8	4	4	7	3	5	6261.7063	0.0010
8	4	4	7	3	4	5908.0477	-0.0001
8	5	4	7	4	4	6556.1622	0.0001
8	5	4	7	4	3	6513.5908	0.0006
8	5	3	7	4	4	6564.3582	0.0008
8	5	3	7	4	3	6521.7857	0.0001

9	0	9	8	1	8	4273.1645	0.0008
9	1	9	8	0	8	4275.3623	0.0056
9	1	8	8	2	7	4541.2756	-0.0062
9	2	8	8	1	7	4609.5784	-0.0015
9	2	7	8	3	6	4550.7279	0.0023
9	3	7	8	2	6	5198.3859	-0.0002
9	4	6	8	3	5	6133.5870	0.0035
9	4	5	8	3	5	6394.2032	0.0007
10	0	10	9	1	9	4732.1008	0.0031
10	0	10	9	0	9	4732.7118	0.0023
10	1	10	9	0	9	4732.9430	0.0015
10	1	10	9	1	9	4732.3259	-0.0038
10	1	9	9	2	8	5016.7790	0.0000
10	2	9	9	1	8	5047.8668	-0.0035
10	3	8	9	2	7	5534.7833	-0.0012
10	4	7	9	3	6	6429.6350	0.0036
10	7	4	10	6	5	3165.1000	0.0139
10	9	2	10	8	3	4196.6309	0.0108
10	9	1	10	8	2	4196.6268	0.0108
11	0	11	10	0	10	5190.8611	0.0000
11	0	11	10	1	10	5190.6291	0.0001
11	1	11	10	0	10	5190.9477	0.0000
11	1	11	10	1	10	5190.7157	0.0000
11	1	10	10	2	9	5482.8358	-0.0062
11	2	10	10	1	9	5496.3816	-0.0002
11	2	9	10	3	8	5695.6610	0.0016
11	3	9	10	2	8	5904.0444	-0.0001
12	0	12	11	1	11	5648.9935	0.0002
12	0	12	11	0	11	5649.0799	0.0000
12	1	12	11	0	11	5649.1120	0.0002
12	1	12	11	1	11	5649.0252	0.0000
12	1	11	11	2	10	5944.3615	0.0002
12	1	11	12	0	12	3318.8719	-0.0010
12	2	11	12	1	12	3320.5080	0.0012
12	2	11	11	1	10	5950.0628	0.0001
12	2	10	11	3	9	6202.1590	0.0018
12	3	10	11	2	9	6306.9496	0.0001
12	10	3	12	9	4	4681.1124	-0.0080
12	10	2	12	9	3	4681.1084	-0.0089
13	0	13	12	0	12	6107.3135	0.0000
13	0	13	12	1	12	6107.2821	0.0005
13	1	13	12	0	12	6107.3256	0.0005
13	1	13	12	1	12	6107.2932	0.0000
13	1	12	12	2	11	6403.8280	-0.0038
13	2	12	12	1	11	6406.1698	-0.0002
14	0	14	13	0	13	6565.5385	0.0000
14	0	14	13	1	13	6565.5267	-0.0002
14	1	14	13	1	13	6565.5311	0.0000
14	1	14	13	0	13	6565.5425	-0.0002

Table S11. Rotational constants of the observed conformers of the TFB dimer calculated at the different levels of theory with deviations from the experimental values.^a

Conformers	Methods	<i>A</i> /MHz	<i>B</i> /MHz	<i>C</i> /MHz	Ave ^b (%)
	Exp.	564.70358	293.04485	266.28527	
I	MP2/6-311++G(2d,p)	560.3(0.8%)	312.5(-6.6%)	280.2(-5.2%)	4.2%
	B3LYP-D3BJ/6-311++G(2d,p)	561.3(0.6%)	304.5(-3.9%)	274.8(-3.2%)	2.6%
	B3LYP-D3BJ/def2-TZVP	564.6(0.0%)	299.5(-2.2%)	271.5(-2.0%)	1.4%
	B2PLYP-D3BJ/6-311++G(2d,p)	560.7(0.7%)	307.3(-4.9%)	276.5(-3.8%)	3.1%
	B2PLYP-D3BJ/def2-TZVP	566.4(-0.3%)	298.2(-1.7%)	270.3(-1.5%)	1.2%
	Exp.	543.64824	271.46605	227.56674	
II	MP2/6-311++G(2d,p)	543.2(0.1%)	286.7(-5.6%)	239.3(-5.2%)	3.6%
	B3LYP-D3BJ/6-311++G(2d,p)	538.4(1.0%)	284.5(-4.8%)	236.7(-4.0%)	3.3%
	B3LYP-D3BJ/def2-TZVP	539.4(0.8%)	280.7(-3.4%)	234.1(-2.9%)	2.4%
	B2PLYP-D3BJ/6-311++G(2d,p)	541.6(0.4%)	283.3(-4.4%)	236.5(-3.9%)	2.9%
	B2PLYP-D3BJ/def2-TZVP	542.9(0.1%)	278.2(-2.5%)	232.6(-2.2%)	1.6%
	Exp.	515.73096	313.29220	250.91942	
IV	MP2/6-311++G(2d,p)	508.4(1.4%)	339.0(-8.2%)	262.8(-4.7%)	4.8%
	B3LYP-D3BJ/6-311++G(2d,p)	509.1(1.3%)	326.3(-4.1%)	259.5(-3.4%)	3.0%
	B3LYP-D3BJ/def2-TZVP	512.4(0.7%)	320.0(-2.1%)	257.1(-2.5%)	1.8%
	B2PLYP-D3BJ/6-311++G(2d,p)	509.3(1.3%)	330.1(-5.3%)	260.5(-3.8%)	3.5%
	B2PLYP-D3BJ/def2-TZVP	516.0(-0.1%)	317.7(-1.4%)	255.8(-1.9%)	1.1%
	Exp.	634.88225	242.50349	192.84574	
V	MP2/6-311++G(2d,p)	644.4(-1.5%)	251.9(-3.9%)	199.8(-3.6%)	3.0%
	B3LYP-D3BJ/6-311++G(2d,p)	637.5(-0.4%)	250.1(-3.1%)	197.7(-2.5%)	2.0%
	B3LYP-D3BJ/def2-TZVP	635.8(-0.1%)	247.3(-2.0%)	195.8(-1.5%)	1.2%
	B2PLYP-D3BJ/6-311++G(2d,p)	642.2(-1.1%)	249.2(-2.7%)	197.6(-2.5%)	2.1%
	B2PLYP-D3BJ/def2-TZVP	638.8(-0.6%)	245.3(-1.2%)	194.8(-1.0%)	0.9%
	Exp.	517.9661	305.1570	229.22660	
XIII	MP2/6-311++G(2d,p)	512.7(1.0%)	333.9(-9.4%)	246.5(-7.5%)	5.3%
	B3LYP-D3BJ/6-311++G(2d,p)	512.2(1.1%)	323.1(-5.9%)	239.5(-4.5%)	3.8%
	B3LYP-D3BJ/def2-TZVP	515.2(0.5%)	311.6(-2.1%)	233.2(-1.7%)	1.5%
	B2PLYP-D3BJ/6-311++G(2d,p)	513.7(0.8%)	324.5(-6.3%)	240.5(-4.9%)	4.0%
	B2PLYP-D3BJ/def2-TZVP	518.8(-0.2%)	306.9(-0.6%)	231.0(-0.8%)	0.5%

^a The values in parentheses are percentage differences defined as: $100\% \times (\text{experimental} - \text{theoretical})/\text{experimental}$.

^b Average absolute percentage error for each level.

Table S12. The decomposition of total interaction energies in kJ mol^{-1} at the SAPT2+(3)/aug-cc-pVDZ level for the six aliphatic alcohol homodimers as well as water homodimer.

	Electrostatics	Induction	Dispersion	Exchange	Total
TFB-I	-58.6(50%) ^a	-19.5(17%)	-38.3(33%)	78.4	-38.0
TFB-II	-49.8(50%)	-17.9(18%)	-32.0(32%)	66.2	-33.5
TFB-IV	-49.1(49%)	-17.0(17%)	-34.2(34%)	68.1	-32.1
TFB-V	-46.8(51%)	-15.4(17%)	-30.3(33%)	62.9	-29.5
TFB-XIII	-48.8(49%)	-17.2(17%)	-33.4(34%)	65.4	-34.0
Methanol dimer ^b	-40.1(59%)	-14.0(20%)	-14.4(21%)	46.8	-21.6
Ethanol dimer ^b	-44.3(55%)	-15.3(19%)	-20.9(26%)	54.7	-25.9
2-Fluoroethanol dimer ^b	-65.6(56%)	-20.6(18%)	-30.7(26%)	84.9	-32.0
TFE dimer ^b	-45.2(54%)	-15.8(19%)	-23.3(28%)	55.2	-29.0
TFP dimer ^b	-56.2(54%)	-20.3(19%)	-27.8(27%)	67.6	-36.7
Water dimer	-35.7(63%)	-11.1(20%)	-9.4(17%)	37.5	-18.6

^a Number in parenthesis refer to the percentage contribution of electrostatic, induction, and dispersion terms to the total attractive interactions.

^b Only the most stable conformers are considered for these five alcohol homodimers.

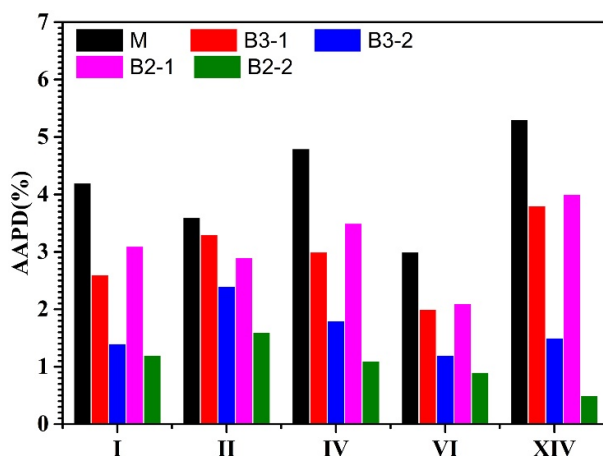


Figure S1. Average absolute percentage deviations (AAPD) between experimental rotational constants (A_0 , B_0 , and C_0) and theoretical values (A_e , B_e , and C_e) calculated at the MP2/6-311++G(2d,p) (M), B3LYP-D3BJ/6-311++G(2d,p) (B3-1), B3LYP-D3BJ/def2-TZVP (B3-2), B2PLYP-D3BJ/6-311++G(2d,p) (B2-1), and B2PLYP-D3BJ/def2-TZVP (B2-2) levels for the five observed TFB dimeric conformers.

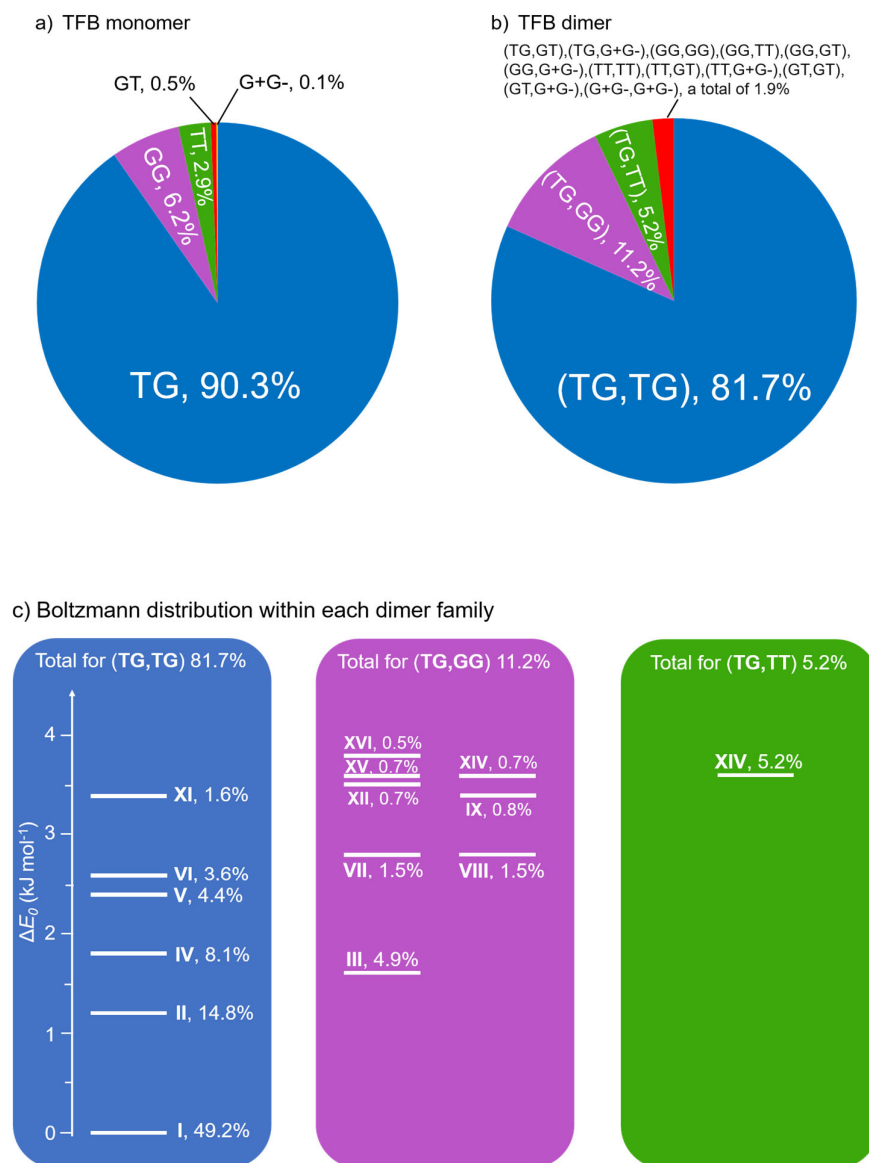


Figure S2. The modified kinetic-thermodynamic model for conformational abundances of the conformers of the TFB dimer in a jet. a) Boltzmann's percentage abundances of the five monomeric TFB families at a temperature of 120 K; b) The percentage abundances of the 15 TFB dimer families based on a kinetic controlled model and the available abundances of the five monomeric TFB families shown in a); c) The 16 most stable conformers in Table 1 are grouped into three TFB dimer family based on their constituents. The relative abundances of binary conformers within each TFB dimer family are calculated based on the Boltzmann distribution at a temperature of 120 K. The final percentage abundance values given take into account of both the Boltzmann distribution within a binary TFB family and the abundances of the specific family. Please see the discussions in the main text. For the predicted percentage abundances of **I:II:IV:V:XIII**, 60%:18%:10%:6%:6%, reported in the main text, we simply re-normalized the percentages of these five observed conformers.

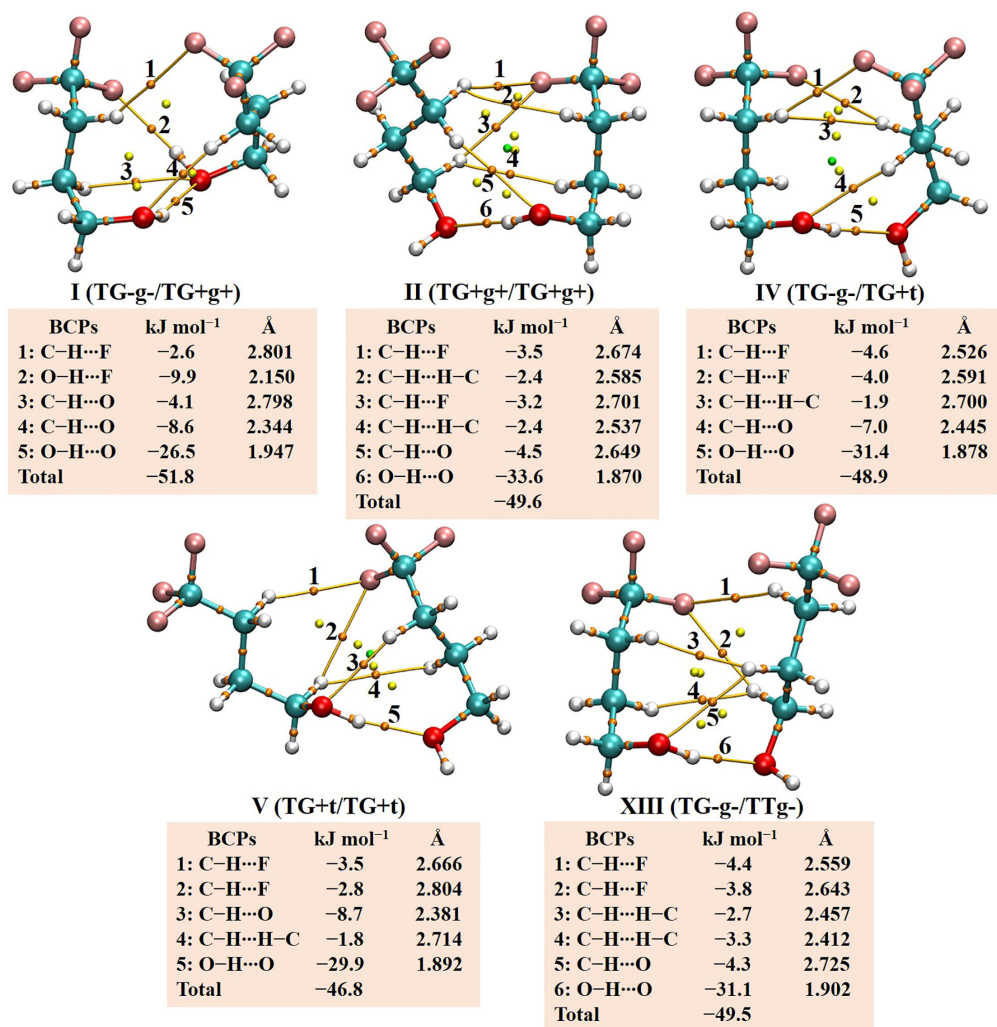


Figure S3. The QTAIM analysis results for the five observed conformers of TFB dimer. The orange and yellow dots indicate the bond critical points and ring critical points, and the green dots denote the cage critical points. The gold lines represent the bond paths. The energetic values of all the NCIs and the corresponding bond distance obtained at the B2PLYP-D3BJ/def2-TZVP level are also given.

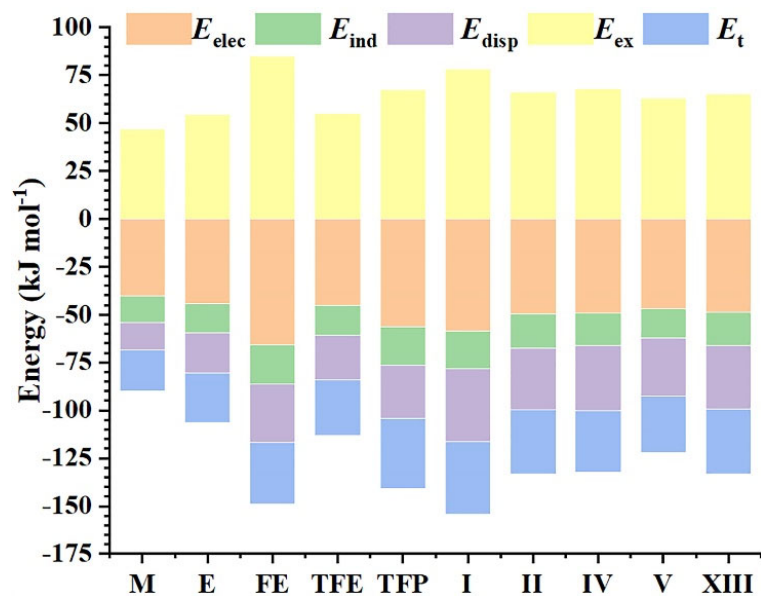


Figure S4. Comparison of the SAPT decompositions of total interaction energy for the most stable conformers of the methanol (M), ethanol (E), 2-fluoroethanol (FE), 2,2,2-trifluoroethanol (TFE), 3,3,3-trifluoro-1-propanol (TFP) dimers with the five observed conformers of TFP dimer, at their respective B3LYP-D3BJ/def2-TZVP geometries.