

Table S1: Calculated spectroscopic constants for  $X^2\Sigma^+$ ,  $1^2\Pi$ ,  $(2)^2\Sigma^+$ ,  $(2)^2\Pi$ ,  $(1)1/2$  and  $(4)1/2$  low-lying states of  $TlF^+$  molecule using different basis sets.

state	$T_e$ ( $\text{cm}^{-1}$ )	$R_e$ ( $\text{\AA}$ )	$\omega_e$ ( $\text{cm}^{-1}$ )	$B_e$ ( $\text{cm}^{-1}$ )	$D_0(\text{ev})$	Ref.	Method	Tl basis	F basis
$X^2\Sigma^+$	0.0	2.029	381.44	0.2355	0.180	This work	MRCI/core,2,0,0,0	ECP68MWB_AVQZ	AVQZ
	0.0	2.060	372.08	0.2283	0.077	This work	MRCI/core 6,2,2,1	ECP60MDF_AV5Z	AVQZ
	0.0	2.159	149.50	0.2050		This work	MRCI/core 4,1,1,0	ECP60MDF_AV5Z	AVQZ
	0.0	2.022	386.60	0.2371	0.207	This work	MRCI/core 1,0,0,0	ECP68MWB_AVQZ	ECP2MWB_AVQZ
	0.0	2.050	349.00		0.020	[34]	MR-AQCC	ECP60MDF	AVQZ
					0.160	[33]	Experimental		
$(1)1/2$	0.0	2.018	399.40	0.2381		This work	MRCI/core,2,0,0,0	ECP68MWB_AVQZ	AVQZ
	0.0	2.012	404.44	0.2395		This work	MRCI/core 1,0,0,0	ECP68MWB_AVQZ	ECP2MWB_AVQZ
$(1)^2\Pi$	456.20	3.123	71.76	0.0993	0.086	This work	MRCI/core,2,0,0,0	ECP68MWB_AVQZ	AVQZ
	559.23	3.093	75.18	0.1013	0.098	This work	MRCI/core 1,0,0,0	ECP68MWB_AVQZ	ECP2MWB_AVQZ
$(2)^2\Sigma^+$	30329.79	2.182	538.10	0.2035	3.347	This work	MRCI/core,2,0,0,0	ECP68MWB_AVQZ	AVQZ
	26550.47	2.247	481.29	0.1919	3.092	This work	MRCI/core 6,2,2,1	ECP60MDF_AV5Z	AVQZ
	30079.84	2.165	597.04	0.2068		This work	MRCI/core 4,1,1,0	ECP60MDF_AV5Z	AVQZ
	30255.99	2.178	540.72	0.2043	3.38	This work	MRCI/core 1,0,0,0	ECP68MWB_AVQZ	ECP2MWB_AVQZ
	29440.00	2.200	517.00			[34]	MR-AQCC	ECP60MDF	AVQZ
$(2)^2\Pi$	53277.73	2.018	411.52	0.2382	0.512	This work	MRCI/core,2,0,0,0	ECP68MWB_AVQZ	AVQZ
	49760.53	2.102	340.51	0.2195	0.216	This work	MRCI/core 6,2,2,1	ECP60MDF_AV5Z	AVQZ
	52412.41	2.056	347.91	0.2293		This work	MRCI/core 4,1,1,0	ECP60MDF_AV5Z	AVQZ
	53272.90	2.013	413.31	0.2392	0.538	This work	MRCI/core 1,0,0,0	ECP68MWB_AVQZ	ECP2MWB_AVQZ
$(4)1/2$	48586.12	2.013	437.85	0.2393		This work	MRCI/core,2,0,0,0	ECP68MWB_AVQZ	AVQZ
	48574.61	2.008	439.06	0.2403		This work	MRCI/core 1,0,0,0	ECP68MWB_AVQZ	ECP2MWB_AVQZ

Table S2: Values of the vibrational energies  $E_v$ , the rotational constants  $B_v$ , the centrifugal distortion constant  $D_v$  and the abscissas of the turning points for the different vibrational levels of spin free states,  $X^2\Sigma^+$ ,  $(2)^2\Sigma^+$ ,  $(1)^2\Pi$  and  $(2)^2\Pi$ , of  $\text{TlF}^+$ .

[Tl<sup>+</sup>: ECP68MWB\_AVQZ, F: all-electron aug-cc-pVQZ].

$X^2\Sigma^+$					
$\nu$	$E_v$ (cm <sup>-1</sup> )	$B_v$ (cm <sup>-1</sup> )	$D_v$ (cm <sup>-1</sup> )	$R_{\min}$ (Å)	$R_{\max}$ (Å)
0	186.02 173.00 <sup>[34]</sup>	0.2328	3.9409(-7)	1.965	2.110
1	535.50 479.00 <sup>[34]</sup>	0.2266	4.8723(-7)	1.928	2.189
2	849.54 733.00 <sup>[34]</sup>	0.2193	6.3232(-7)	1.906	2.259
3	1124.21	0.2105	8.7127(-7)	1.891	2.334
4	1355.21	0.1995	1.2947(-6)	1.880	2.421
5	1538.24	0.1852	2.1364(-6)	1.872	2.531
6	1669.19	0.1652	4.8065(-6)	1.867	2.689
7	1732.40	0.1132	2.7945(-5)	1.864	3.392
$(1)^2\Pi$					
$\nu$	$E_v$ (cm <sup>-1</sup> )	$B_v$ (cm <sup>-1</sup> )	$D_v$ (cm <sup>-1</sup> )	$R_{\min}$ (Å)	$R_{\max}$ (Å)
0	36.06	0.0982	7.4418(-7)	2.977	3.306
1	106.44	0.0961	8.0782(-7)	2.882	3.459
2	172.82	0.0932	9.5702(-7)	2.825	3.595
3	233.87	0.0903	9.5244(-7)	2.783	3.722
4	290.79	0.0868	1.1649(-6)	2.752	3.852
5	342.29	0.0829	1.3071(-6)	2.728	3.996
6	388.32	0.0785	1.4099(-6)	2.709	4.145
7	429.37	0.0743	1.6620(-6)	2.693	4.319
8	465.58	0.0702	1.2808(-6)	2.680	4.486
9	499.24	0.0677	1.3217(-6)	2.669	4.642
10	530.43	0.0637	1.7136(-6)	2.659	4.826
11	558.40	0.0606	1.2198(-6)	2.651	4.998
12	584.70	0.0580	1.5986(-6)	2.643	5.173
13	608.76	0.0545	1.9696(-6)	2.636	5.366
14	629.90	0.0503	2.5835(-6)	2.630	5.607
15	647.70	0.0460	2.4114(-6)	2.626	5.887
$(2)^2\Sigma^+$					
$\nu$	$E_v$ (cm <sup>-1</sup> )	$B_v$ (cm <sup>-1</sup> )	$D_v$ (cm <sup>-1</sup> )	$R_{\min}$ (Å)	$R_{\max}$ (Å)
0	268.32	0.2032	1.1723(-7)	2.124	2.244
1	802.61	0.2026	1.1862(-7)	2.084	2.293

2	1333.16	0.2020	1.1996(-7)	2.057	2.327
3	1859.96	0.2013	1.2124(-7)	2.036	2.356
4	2383.04	0.2007	1.2248(-7)	2.018	2.383
5	2902.40	0.2000	1.2365(-7)	2.002	2.407
6	3418.06	0.1993	1.2478(-7)	1.988	2.429
7	3930.03	0.1986	1.2584(-7)	1.975	2.450
8	4438.33	0.1979	1.2688(-7)	1.963	2.471
9	4942.98	0.1972	1.2802(-7)	1.952	2.491
10	5443.95	0.1964	1.2915(-7)	1.942	2.510
11	5941.20	0.1957	1.3001(-7)	1.932	2.528
12	6434.78	0.1949	1.3082(-7)	1.923	2.547
13	6924.72	0.1941	1.3187(-7)	1.915	2.564
14	7411.00	0.1934	1.3280(-7)	1.907	2.582
15	7893.61	0.1926	1.3358(-7)	1.899	2.599
16	8372.57	0.1918	1.3451(-7)	1.891	2.616
17	8847.88	0.1910	1.3540(-7)	1.884	2.633
18	9319.53	0.1901	1.3621(-7)	1.877	2.650
19	9787.52	0.1893	1.3707(-7)	1.871	2.667
20	10251.84	0.1884	1.3791(-7)	1.865	2.683
21	10712.50	0.1876	1.3875(-7)	1.859	2.699
22	11169.49	0.1867	1.3959(-7)	1.853	2.716
23	11622.80	0.1859	1.4043(-7)	1.847	2.732
24	12072.42	0.1850	1.4126(-7)	1.842	2.748
25	12518.35	0.1841	1.4208(-7)	1.836	2.764
26	12960.58	0.1832	1.4299(-7)	1.831	2.780
27	13399.10	0.1823	1.4399(-7)	1.826	2.796
28	13833.88	0.1814	1.4507(-7)	1.821	2.813
29	14264.89	0.1804	1.4608(-7)	1.817	2.829
30	14692.10	0.1795	1.4703(-7)	1.812	2.845
31	15115.51	0.1785	1.4798(-7)	1.808	2.861
32	15535.09	0.1776	1.4898(-7)	1.803	2.877
33	15950.84	0.1766	1.5006(-7)	1.799	2.893
34	16362.72	0.1756	1.5129(-7)	1.795	2.910
35	16770.71	0.1746	1.5266(-7)	1.791	2.926
36	17174.75	0.1736	1.5427(-7)	1.787	2.942
37	17574.79	0.1726	1.5615(-7)	1.784	2.959
38	17970.75	0.1715	1.5817(-7)	1.780	2.976
39	18362.55	0.1705	1.6028(-7)	1.776	2.992
40	18750.11	0.1694	1.6257(-7)	1.773	3.009
41	19133.33	0.1682	1.6503(-7)	1.770	3.026
42	19512.12	0.1671	1.6750(-7)	1.766	3.044
43	19886.40	0.1659	1.6996(-7)	1.763	3.061
44	20256.08	0.1647	1.7334(-7)	1.760	3.079
45	20621.02	0.1635	1.7850(-7)	1.757	3.097
46	20980.99	0.1622	1.8383(-7)	1.754	3.116
47	21335.77	0.1609	1.8795(-7)	1.751	3.134

48	21685.19	0.1595	1.9397(-7)	1.748	3.153
49	22029.02	0.1581	2.0265(-7)	1.745	3.173
50	22366.89	0.1565	2.1021(-7)	1.743	3.193
51	22698.51	0.1549	2.2096(-7)	1.740	3.214
52	23023.44	0.1532	2.3517(-7)	1.738	3.236
53	23341.11	0.1514	2.4685(-7)	1.735	3.259
54	23651.12	0.1494	2.6343(-7)	1.733	3.282
55	23952.87	0.1473	2.8371(-7)	1.731	3.307
56	24245.63	0.1450	3.0841(-7)	1.729	3.334
57	24528.60	0.1425	3.3365(-7)	1.727	3.362
58	24800.97	0.1397	3.6886(-7)	1.725	3.393
(2) <sup>2</sup> Π					
$\nu$	$E_\nu$ (cm <sup>-1</sup> )	$B_\nu$ (cm <sup>-1</sup> )	$D_\nu$ (cm <sup>-1</sup> )	$R_{\min}$ (Å)	$R_{\max}$ (Å)
0	203.61	0.2363	3.2833(-7)	1.955	2.093
1	599.59	0.2325	3.4835(-7)	1.915	2.159
2	979.91	0.2286	3.7042(-7)	1.891	2.211
3	1344.47	0.2246	3.9474(-7)	1.873	2.258
4	1693.16	0.2204	4.2194(-7)	1.858	2.304
5	2025.88	0.2161	4.5252(-7)	1.846	2.348
6	2342.48	0.2116	4.8906(-7)	1.836	2.393
7	2642.63	0.2069	5.3791(-7)	1.827	2.438
8	2925.54	0.2018	5.8789(-7)	1.819	2.486
9	3191.21	0.1968	6.0235(-7)	1.812	2.534
10	3441.60	0.1918	6.7747(-7)	1.806	2.584
11	3675.59	0.1860	7.5762(-7)	1.800	2.637
12	3892.90	0.1807	7.5137(-7)	1.796	2.694
13	4096.45	0.1757	6.2805(-7)	1.791	2.753
14	4197.07	0.0505	9.3407(-7)	1.789	2.782
15	4219.70	0.0479	1.0335(-6)	1.788	2.787

Note: Figures in parentheses for 10 to the power.

Table S3: Values of the vibrational energies  $E_v$ , the rotational constants  $B_v$ , the centrifugal distortion constant  $D_v$ , and the abscissas of the turning points  $R_{min}$  and  $R_{max}$  for the different vibrational levels of spin-orbit states, (1)1/2, (1)3/2, (3)1/2, (4)1/2 and (2)3/2, of TlF<sup>+</sup>. [Tl<sup>+</sup>: ECP68MWB\_AVQZ, F: all-electron aug-cc-pVQZ].

(1) 1/2					
$\nu$	$E_v$ (cm <sup>-1</sup> )	$B_v$ (cm <sup>-1</sup> )	$D_v$ (cm <sup>-1</sup> )	$R_{min}$ (Å)	$R_{max}$ (Å)
0	195.11	0.2355	3.6785(-7)	1.956	2.097
1	564.06	0.2298	4.4436(-7)	1.918	2.172
2	899.54	0.2232	5.6000(-7)	1.896	2.238
3	1197.80	0.2152	7.4391(-7)	1.881	2.306
4	1454.60	0.2054	1.0560(-6)	1.869	2.383
5	1664.85	0.1916	1.3627(-6)	1.861	2.477
(1) 3/2					
$\nu$	$E_v$ (cm <sup>-1</sup> )	$B_v$ (cm <sup>-1</sup> )	$D_v$ (cm <sup>-1</sup> )	$R_{min}$ (Å)	$R_{max}$ (Å)
0	35.49	0.0983	7.7731(-7)	2.973	3.305
1	104.25	0.0959	8.2210(-7)	2.881	3.466
2	169.48	0.0932	8.8981(-7)	2.825	3.598
3	230.65	0.0901	9.8687(-7)	2.785	3.726
4	287.25	0.0867	1.1184(-6)	2.754	3.856
5	338.82	0.0828	1.3082(-6)	2.730	3.996
6	384.79	0.0782	1.6972(-6)	2.711	4.136
7	423.77	0.0717	3.0004(-6)	2.696	4.299
(3) 1/2					
$\nu$	$E_v$ (cm <sup>-1</sup> )	$B_v$ (cm <sup>-1</sup> )	$D_v$ (cm <sup>-1</sup> )	$R_{min}$ (Å)	$R_{max}$ (Å)
0	267.19	0.2027	1.1736(-7)	2.127	2.247
1	799.20	0.2021	1.1888(-7)	2.086	2.295
2	1327.28	0.2015	1.2036(-7)	2.059	2.330
3	1851.44	0.2008	1.2179(-7)	2.038	2.360
4	2371.67	0.2002	1.2315(-7)	2.020	2.386
5	2887.97	0.1995	1.2444(-7)	2.004	2.410
6	3400.35	0.1988	1.2574(-7)	1.990	2.433
7	3908.81	0.1981	1.2701(-7)	1.977	2.454
8	4413.32	0.1974	1.2817(-7)	1.965	2.475
9	4913.91	0.1966	1.2937(-7)	1.955	2.495
10	5410.56	0.1959	1.3051(-7)	1.944	2.514
11	5903.28	0.1951	1.3160(-7)	1.935	2.533
12	6392.07	0.1943	1.3270(-7)	1.926	2.551
13	6876.92	0.1935	1.3369(-7)	1.917	2.569
14	7357.85	0.1927	1.3469(-7)	1.909	2.587
15	7834.87	0.1919	1.3561(-7)	1.901	2.604
16	8307.98	0.1911	1.3649(-7)	1.894	2.622

17	8777.21	0.1903	1.3723(-7)	1.887	2.639
18	9242.60	0.1895	1.3791(-7)	1.880	2.655
19	9704.17	0.1887	1.3840(-7)	1.873	2.672
20	10162.00	0.1878	1.3871(-7)	1.867	2.689
21	10616.14	0.1870	1.3873(-7)	1.861	2.705
22	11066.72	0.1862	1.3838(-7)	1.855	2.721
23	11513.87	0.1854	1.3749(-7)	1.849	2.737
24	11957.77	0.1846	1.3590(-7)	1.844	2.753
25	12398.70	0.1839	1.3340(-7)	1.839	2.769
26	12836.97	0.1832	1.2985(-7)	1.833	2.784
27	13273.01	0.1826	1.2521(-7)	1.828	2.799
28	13707.30	0.1820	1.1976(-7)	1.823	2.814
29	14140.39	0.1816	1.1425(-7)	1.819	2.828
30	14572.77	0.1812	1.0998(-7)	1.814	2.842
31	15004.78	0.1808	1.0881(-7)	1.809	2.855
32	15436.43	0.1804	1.1299(-7)	1.805	2.868
33	15867.24	0.1799	1.2504(-7)	1.800	2.880
34	16296.04	0.1792	1.4749(-7)	1.796	2.894
35	16720.78	0.1781	1.8155(-7)	1.792	2.908
36	17138.61	0.1765	2.2241(-7)	1.788	2.925
37	17546.41	0.1745	2.5128(-7)	1.784	2.943
38	17942.41	0.1723	2.4342(-7)	1.780	2.962
39	18327.77	0.1705	2.1242(-7)	1.777	2.982
40	18705.12	0.1690	2.0578(-7)	1.773	3.002

(4) 1/2

$\nu$	$E_\nu$ (cm <sup>-1</sup> )	$B_\nu$ (cm <sup>-1</sup> )	$D_\nu$ (cm <sup>-1</sup> )	$R_{\min}$ (Å)	$R_{\max}$ (Å)
0	216.95	0.2376	2.9198(-7)	1.952	2.086
1	641.13	0.2343	3.0485(-7)	1.913	2.148
2	1051.74	0.2309	3.1862(-7)	1.889	2.196
3	1448.73	0.2275	3.3338(-7)	1.870	2.240
4	1832.08	0.2239	3.4935(-7)	1.856	2.281
5	2201.73	0.2203	3.6792(-7)	1.843	2.320
6	2557.42	0.2165	3.9179(-7)	1.833	2.359
7	2898.60	0.2126	4.1246(-7)	1.823	2.399
8	3225.55	0.2087	4.0987(-7)	1.815	2.438
9	3540.42	0.2050	4.3480(-7)	1.808	2.477
10	3842.65	0.2009	4.7783(-7)	1.801	2.517
11	4131.19	0.1969	4.6597(-7)	1.795	2.558
12	4407.89	0.1928	5.2006(-7)	1.789	2.599
13	4671.79	0.1888	4.9672(-7)	1.784	2.641
14	4924.81	0.1848	5.2628(-7)	1.780	2.684
15	5167.47	0.1813	4.6025(-7)	1.775	2.727

(2) 3/2

0	186.82	0.2330	3.7718(-7)	1.966	2.110
1	547.49	0.2286	4.0892(-7)	1.926	2.181

2	889.99	0.2239	4.4497(-7)	1.902	2.239
3	1214.14	0.2191	4.8723(-7)	1.884	2.292
4	1519.63	0.2140	5.4187(-7)	1.869	2.344
5	1805.68	0.2085	6.0528(-7)	1.858	2.398
6	2072.04	0.2029	6.4246(-7)	1.848	2.451
7	2320.58	0.1971	7.4617(-7)	1.840	2.507
8	2508.37	0.0708	8.4258(-7)	1.834	2.555
9	2548.64	0.0687	9.1126(-7)	1.833	2.566

Note: Figures in parentheses for 10 to the power.

Table S4: Calculated FCFs of TlF<sup>+</sup> for the (2)<sup>2</sup>Π (ν') – X<sup>2</sup>Σ<sup>+</sup> (ν'') transition using different core potentials for Tl<sup>+</sup> and for the (2)<sup>2</sup>Π<sub>1/2</sub> (ν') – X<sup>2</sup>Σ<sup>+</sup><sub>1/2</sub> (ν'') transition using ECP60MDF for Tl<sup>+</sup>.

[Tl <sup>+</sup> : ECP68MWB_AVQZ, F: all-electron aug-cc-pVQZ]						
(2) <sup>2</sup> Π (ν') – X <sup>2</sup> Σ <sup>+</sup> (ν'')						
	ν' = 0	1	2	3	4	5
ν'' = 0	<b>9.77(-1)</b>	2.20(-2)	7.32(-4)	7.15(-5)	8.26(-8)	1.48(-7)
1	2.26(-2)	<b>8.95(-1)</b>	7.62(-2)	5.86(-3)	6.55(-4)	1.39(-5)
2	2.45(-4)	7.98(-2)	<b>7.13(-1)</b>	1.75(-1)	2.77(-2)	4.36(-3)
3	6.67(-6)	3.28(-3)	1.84(-1)	4.07(-1)	2.86(-1)	9.23(-2)
4	3.38(-6)	1.25(-4)	2.27(-2)	2.86(-1)	8.46(-2)	2.78(-1)
5	2.15(-6)	1.27(-5)	2.58(-3)	8.61(-2)	2.21(-1)	1.62(-2)
[Tl <sup>+</sup> : ECP60MDF_AV5Z, F: all-electron aug-cc-pVQZ, MRCI/core,6,2,2,1]						
(2) <sup>2</sup> Π (ν') – X <sup>2</sup> Σ <sup>+</sup> (ν'')						
	ν' = 0	1	2	3	4	5
ν'' = 0	<b>8.89(-1)</b>	9.37(-2)	1.46(-2)	2.44(-3)	3.54(-4)	4.54(-5)
1	1.11(-1)	<b>7.34(-1)</b>	1.12(-1)	3.34(-2)	7.95(-3)	1.95(-3)
2	5.20(-5)	1.70(-1)	<b>6.75(-1)</b>	9.04(-2)	4.82(-2)	1.12(-2)
3	2.99(-4)	1.99(-3)	1.61(-1)	7.32(-1)	8.79(-3)	
[Tl <sup>+</sup> : ECP60MDF_AV5Z, F: all-electron aug-cc-pVQZ, MRCI/core,6,2,2,1]						
(2) <sup>2</sup> Π <sub>1/2</sub> (ν') – X <sup>2</sup> Σ <sup>+</sup> <sub>1/2</sub> (ν'')						
	ν' = 0	1	2	3		
ν'' = 0	<b>9.11(-1)</b>	8.25(-2)	5.68(-2)	5.31(-4)		
1	8.56(-2)	<b>7.41(-1)</b>	1.35(-1)	2.78(-2)		
2	3.20(-3)	1.65(-1)	4.65(-1)	2.15 (-1)		
3	4.41(-5)	1.12(-2)	3.45(-1)	1.50 (-1)		

Note: The figures in parentheses for 10 to the power.



Table S5: Calculated FCFs of TlF<sup>+</sup> for the (2)<sup>2</sup>Σ<sup>+</sup> – X<sup>2</sup>Σ<sup>+</sup> and (1)<sup>2</sup>Π – X<sup>2</sup>Σ<sup>+</sup> transitions.  
 [Tl<sup>+</sup>: ECP68MWB\_AVQZ, F: all-electron aug-cc-pVQZ].

(2) <sup>2</sup> Σ <sup>+</sup> (ν') – X <sup>2</sup> Σ <sup>+</sup> (ν'')						
	ν' = 0	1	2	3	4	5
ν'' = 0	1.21(-1)	1.57(-1)	1.70(-1)	1.52(-1)	1.24(-1)	9.32(-2)
1	4.75(-1)	8.26(-2)	1.37(-2)	5.24(-3)	3.06(-2)	5.84(-2)
2	3.66(-1)	2.01(-1)	4.69(-2)	7.94(-2)	5.89(-3)	6.73(-6)
3	5.63(-3)	4.47(-1)	1.73(-1)	2.32(-4)	1.31(-1)	3.40(-3)
4	2.45(-2)	1.33(-2)	2.69(-1)	1.82(-1)	2.57(-2)	2.12(-1)
5	3.04(-3)	2.96(-2)	1.57(-1)	1.10(-2)	4.86(-2)	1.00(-2)
(1) <sup>2</sup> Π (ν') – X <sup>2</sup> Σ <sup>+</sup> (ν'')						
	ν' = 0	1	2	3	4	5
ν'' = 0	2.69(-19)	3.86(-18)	2.64(-17)	1.17(-16)	3.82(-16)	9.76(-16)
1	2.50(-16)	3.21(-15)	1.99(-14)	8.15(-14)	2.46(-13)	5.88(-13)
2	1.43(-13)	1.60(-12)	8.83(-12)	3.24(-11)	8.89(-11)	1.95(-10)
3	6.82(-11)	6.34(-10)	2.96(-9)	9.46(-9)	2.29(-8)	4.53(-8)
4	2.99(-8)	2.11(-7)	7.86 (-7)	2.06(-6)	4.24(-6)	7.27 (-6)
5	1.22(-5)	5.54(-5)	1.45(-5)	2.90 (-4)	4.73(-4)	6.69(-4)

Note: Figures in parentheses for 10 to the power.

Table S6: Calculated FCFs corresponding to transitions between the vibrational levels of TIF<sup>+</sup> with (2)<sup>2</sup>Π (ν′ = 0, 1) and (2)<sup>2</sup>Π<sub>1/2</sub> (ν′ = 0, 1) as the higher levels to the levels of (2)<sup>2</sup>Σ<sup>+</sup>, (1)<sup>2</sup>Π and (2)<sup>2</sup>Σ<sup>+</sup><sub>1/2</sub>. [TI<sup>+</sup>: ECP68MWB\_AVQZ, F: all-electron aug-cc-pVQZ]

	(2) <sup>2</sup> Π(ν′) - (2) <sup>2</sup> Σ <sup>+</sup> (ν″)		(2) <sup>2</sup> Π(ν′) - (1) <sup>2</sup> Π(ν″)		(2) <sup>2</sup> Π <sub>1/2</sub> (ν′) - (2) <sup>2</sup> Σ <sup>+</sup> <sub>1/2</sub> (ν″)	
	ν′ = 0	1	ν′ = 0	1	ν′ = 0	1
ν″ = 0	5.66(-2)	2.72(-1)	1.84(-22)	3.56(-20)	3.69(-2)	1.99(-1)
1	1.10(-1)	1.80(-1)	3.26(-21)	6.01(-19)	8.62(-2)	1.93(-1)
2	1.44(-1)	7.16(-2)	2.69(-20)	4.75(-18)	1.26(-1)	1.05(-1)
3	1.52(-1)	8.85(-3)	1.40(-19)	2.39(-17)	1.45(-1)	2.83(-2)
4	1.39(-1)	2.79(-3)	5.27(-19)	8.72(-17)	1.43(-1)	2.70(-4)
5	1.16(-1)	2.58(-2)	1.52(-18)	2.45(-16)	1.26(-1)	1.15(-2)
6	8.99(-2)	5.21(-2)	3.54(-18)	5.55(-16)	1.02(-1)	3.79(-2)
7	6.54(-2)	6.80(-2)	7.09(-18)	1.08(-15)	7.71(-2)	6.04(-2)
8	4.53(-2)	7.12(-2)	1.24(-17)	1.87(-15)	5.52(-2)	7.11(-2)
9	3.01(-2)	6.48(-2)	2.17(-17)	3.22(-15)	3.77(-2)	7.03(-2)
10	1.93(-2)	5.35(-2)	3.30(-17)	4.81(-15)	2.48(-2)	6.16(-2)
11	1.20(-2)	4.10(-2)	4.85(-17)	6.97(-15)	1.57(-2)	4.95(-2)
12	7.32(-3)	2.97(-2)	6.98(-17)	9.91(-15)	9.69(-3)	3.72(-2)
13	4.35(-3)	2.05(-2)	9.17(-17)	1.28(-14)	5.83(-3)	2.65(-2)
14	2.53(-3)	1.36(-2)	1.08(-16)	1.51(-14)	3.49(-3)	1.85(-2)
15	1.44(-3)	8.76(-3)	1.20(-16)	1.65(-14)		
16	8.15(-4)	5.47(-3)	1.31(-16)	1.79(-14)		
17	4.52(-4)	3.33(-3)	1.34(-16)	1.82(-14)		
18	2.48(-4)	1.99(-3)	1.31(-16)	1.77(-14)		
19	1.34(-4)	1.16(-3)	1.32(-16)	1.78(-14)		
20	7.22(-5)	6.74(-4)	1.32(-16)	1.77(-14)		
21	3.84(-5)	3.83(-4)	1.30(-16)	1.73(-14)		
22	2.03(-5)	2.15(-4)	1.23(-16)	1.64(-14)		
23	1.06(-5)	1.19(-4)	1.12(-16)	1.49(-14)		
24	5.55(-6)	6.56(-5)	9.97(-17)	1.31(-14)		
25	2.87(-6)	3.57(-5)				
26	1.48(-6)	1.93(-5)				
27	7.62(-7)	1.03(-5)				
28	3.90(-7)	5.54(-6)				
29	1.99(-7)	2.94(-6)				
30	1.01(-7)	1.55(-6)				
31	5.17(-8)	8.20(-7)				
32	2.62(-8)	4.31(-7)				
33	1.33(-8)	2.25(-7)				
34	6.77(-9)	1.18(-7)				
35	3.43(-9)	6.16(-8)				
36	1.74(-9)	3.21(-8)				

37	8.81(-10)	1.67(-8)
38	4.47(-10)	8.73(-9)
39	2.27(-10)	4.54(-9)
40	1.15(-10)	2.37(-9)
41	5.92(-11)	1.23(-9)
42	3.04(-11)	6.48(-10)
43	1.57(-11)	3.40(-10)
44	8.12(-12)	1.79(-10)
45	4.20(-12)	9.47(-11)
46	2.17(-12)	5.01(-11)
47	1.12(-12)	2.66(-11)
48	5.84(-13)	1.41(-11)
49	3.03(-13)	7.55(-12)
50	1.59(-13)	4.04(-12)
51	8.46(-14)	2.17(-12)
52	4.569(-14)	1.18(-12)
53	2.51(-14)	6.50(-13)
54	1.41(-14)	3.63(-13)
55	8.09(-15)	2.06(-13)
56	4.71(-15)	1.19(-13)

Note: Figures in parentheses for 10 to the power.