Study of Millimeter-Wave Rotational Spectra of Phosphorus Trifluoride in Ground, $v_2 = 1$ and $v_4 = 1$ States

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Abstract: The millimeter-wave rotational spectra of the ground and excited vibrational states $v_2 = 1$ and $v_4 = 1$ of the symmetric top molecule, PF_3 , have been analyzed again. The $B_0 = 7819.9907(13)$ MHz, $D_J = 7.84984(41)$ kHz, $D_{JK} = -11.7644$ (11) kHz, $H_J = 15.678$ (36) mHz, $H_{JK} = -66.46$ (12) mHz and $H_{KJ} = 87.42$ (15) mHz have been determined for ground state. The $l = \pm 1$ series have been assigned and the rotational parameters including $B_4 = 7823.09212(41)$ MHz, $(q^+)_4 = -29.49200(65)$ MHz, $r_1 = 2.9465$ (13) MHz and $(C\zeta)_4 = -3010.94684(41)$ MHz for $v_4 = 1$ state were determined accurately.

Keywords: Millimeter-wave rotational spectra, Excited vibrational state, Symmetric top molecules, PF_3

Introduction

Phosphorus trifluoride (PF_3) has one threefold axis of symmetry (C_3) and three vertical planes of symmetry (σ_v). This molecule, therefore, belongs to the spectroscopic group C_{3v} . Selection rules for a molecule of this configuration show that there should be two totally symmetric fundamentals (Type A_1) and two doubly degenerate fundamentals (Type E).

Several authors have studied the rotational spectra of the ground state and some excited states¹⁻¹⁰. The lowest doubly degenerate vibrational level, $v_4 = 1$, lies at 344 cm^{-1} (Deg deform). The next highest frequency, v_2 , is found at 487 cm^{-1} (Sym deform)¹¹. There is no doubt about the assignment of the series of lines which lie to high frequency of the ground state rotational transitions. Owing to the large dipole moment and the large thermal population, the spectra are intense. The aim of this study is determination of rotational parameters for mixing the low and high J values in ground and $v_2 = 1$ and $v_4 = 1$ states, which are more accurate and reliable.

Spectra in the ground and $v_2=1$ states

The rovibrational Hamiltonian for a non-degenerate vibrational state is essentially similar to that of the ground state. The transition frequencies for $J \rightarrow (J+1)$ can be expressed as

$$\begin{aligned} \nu = & 2B(J+1) - 4D_J(J+1)^3 - 2D_{JK}(J+1)k^2 + H_J(J+1)^3[(J+2)^3 - J^3] \\ & + 4H_{JK}(J+1)^3k^2 + 2H_{KJ}(J+1)k^4 + \dots \end{aligned} \quad (1)$$

We have mixed the 181 frequencies of Refs 5 and 7 in order to improve the accuracy of the rotational and other centrifugal distortion constants. Then a weighted least-squares method¹² was used to fit the mixed frequencies for low and high J values to the parameters of equation 1, in which the weights were taken to be $w = 1/(\text{observed error})^2 = 1/(0.2)^2$, where 0.2 in MHz is estimated uncertainty in an observation for each unblended line.

The fit to the transitions are given in Table 1 and the constants obtained are given in Table 5. Some of the lines have an observed error of 0.3 to 0.9 MHz to allow for overlapping or broadening. These Tables show that the mixed frequencies of low and high J values of PF_3 were fitted very well and correlation coefficients of parameters are reasonable (Table 2). The structural parameters of this compound as shown in Table 5 were obtained with higher accuracy and compared with previous work.

Table 1. Results of Refinement of Observed Frequencies for PF_3 in ground State.

S.No.	J	K	Fobs/MHz	Calc/MHz	(Obs-Calc)/MHz	Error/MHz
1	0	0	15639.9500	15639.9501	-0.0001	0.0500
2	1	0	31279.8400	31279.7118	0.1282	0.1500
3	5	5	93836.6880	93836.6360	0.0520	0.2000
4	5	4	93835.5070	93835.3656	0.1414	0.2000
5	5	3	93834.4280	93834.3776	0.0504	0.2000
6	5	2	93833.7210	93833.6720	0.0490	0.2000
7	5	1	93833.3120	93833.2486	0.0634	0.3000
8	5	0	93833.3120	93833.1075	0.2045	0.3000
9	6	6	109475.0750	109475.0297	0.0453	0.2000
10	6	5	109473.2610	109473.2182	0.0428	0.2000
11	6	4	109471.7940	109471.7362	0.0578	0.2000
12	6	3	109470.6510	109470.5837	0.0673	0.2000
13	6	2	109469.8450	109469.7606	0.0844	0.3000
14	6	1	109469.2400	109469.2667	-0.0267	0.3000
15	6	0	109469.2400	109469.1021	0.1379	0.2000
16	7	7	125113.0790	125112.9986	0.0804	0.2000
17	7	6	125110.6360	125110.5519	0.0841	0.3000
18	7	5	125108.5650	125108.4819	0.0831	0.2000
19	7	4	125106.8910	125106.7885	0.1025	0.2000
20	7	3	125105.5770	125105.4716	0.1054	0.2000
21	7	2	125104.6590	125104.5310	0.1280	0.2000
22	7	1	125103.9900	125103.9667	0.0233	0.3000
23	7	0	125103.9900	125103.7786	0.2114	0.3000
24	8	8	140750.4000	140750.4956	-0.0956	0.4000
25	8	7	140747.3100	140747.3195	-0.0095	0.3000
26	8	6	140744.5950	140744.5674	0.0276	0.3000
27	8	5	140742.2780	140742.2391	0.0389	0.3000
28	8	4	140740.3800	140740.3344	0.0456	0.3000
29	8	3	140738.8950	140738.8532	0.0418	0.3000
30	8	2	140737.8600	140737.7953	0.0647	0.3000
31	8	1	140737.1100	140737.1605	-0.0505	0.4000
32	8	0	140737.1100	140736.9490	0.1610	0.4000
33	10	10	172024.3310	172023.8847	0.4463	0.4000

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34	10	9	172019.0420	172018.9673	0.0747	0.2000
35	10	8	172014.6220	172014.5687	0.0533	0.3000
36	10	7	172010.7420	172010.6885	0.0535	0.3000
37	10	6	172007.4010	172007.3263	0.0747	0.3000
38	10	5	172004.5480	172004.4819	0.0661	0.3000
39	10	4	172002.3890	172002.1551	0.2339	0.3000
40	10	3	172000.3890	172000.3455	0.0435	0.3000
41	10	2	171999.1010	171999.0530	0.0480	0.3000
42	10	1	171998.1790	171998.2776	-0.0986	0.4000
43	10	0	171998.1790	171998.0192	0.1598	0.4000
44	11	0	187625.6270	187625.5434	0.0836	0.2000
45	11	1	187625.9360	187625.8253	0.1107	0.2000
46	11	2	187626.7700	187626.6710	0.0990	0.2000
47	11	3	187628.1780	187628.0805	0.0975	0.2000
48	11	4	187630.1500	187630.0541	0.0959	0.2000
49	11	5	187632.6860	187632.5919	0.0941	0.2000
50	11	6	187635.7890	187635.6940	0.0950	0.2000
51	11	7	187639.4580	187639.3609	0.0971	0.2000
52	11	8	187643.6950	187643.5927	0.1023	0.2000
53	11	9	187648.4960	187648.3900	0.1060	0.2000
54	11	10	187653.8590	187653.7530	0.1060	0.2000
55	13	10	218906.6270	218906.5237	0.1033	0.4000
56	13	9	218900.5120	218900.2705	0.2415	0.4000
57	13	8	218894.9120	218894.6770	0.2350	0.4000
58	13	7	218889.9280	218889.7428	0.1852	0.4000
59	13	6	218885.6380	218885.4673	0.1707	0.4000
60	13	5	218882.0540	218881.8502	0.2038	0.4000
61	13	4	218879.0980	218878.8913	0.2067	0.4000
62	13	3	218876.7230	218876.5901	0.1329	0.4000
63	13	2	218875.2450	218874.9466	0.2984	0.2000
64	13	1	218874.1700	218873.9605	0.2095	0.6000
65	13	0	218874.1700	218873.6318	0.5382	0.6000
66	14	14	234563.0160	234562.9209	0.0951	0.5000
67	14	13	234553.6320	234553.3901	0.2419	0.5000
68	14	12	234544.8240	234544.5687	0.2553	0.5000
69	14	10	234529.3200	234529.0509	0.2691	0.5000
70	14	8	234516.3600	234516.3622	-0.0022	0.5000
71	14	7	234511.0800	234511.0772	0.0028	0.5000
72	14	6	234506.5060	234506.4979	0.0081	0.5000
73	14	5	234502.7280	234502.6237	0.1043	0.5000
74	14	4	234499.5060	234499.4544	0.0516	0.5000
75	14	3	234497.1840	234496.9897	0.1943	0.5000
76	14	2	234495.4320	234495.2294	0.2026	0.5000
77	14	1	234494.2320	234494.1732	0.0588	0.7000
78	14	0	234494.2320	234493.8212	0.4108	0.7000
79	15	0	250111.2750	250111.1910	0.0840	0.7000
80	15	15	250195.9200	250195.7914	0.1286	0.2000
81	15	14	250185.0110	250184.8714	0.1396	0.2000
82	15	13	250174.8270	250174.7088	0.1182	0.2000
83	15	12	250165.4220	250165.3026	0.1194	0.2000
84	15	11	250156.7800	250156.6520	0.1280	0.2000
85	15	10	250148.8810	250148.7562	0.1248	0.2000
86	15	9	250141.7300	250141.6145	0.1155	0.2000
87	15	8	250135.3340	250135.2263	0.1077	0.2000
88	15	7	250129.6360	250129.5909	0.0451	0.5000
89	15	6	250124.8000	250124.7080	0.0920	0.5000
90	15	5	250120.7080	250120.5770	0.1310	0.5000
91	15	4	250117.3100	250117.1977	0.1123	0.5000
92	15	3	250114.6360	250114.5696	0.0664	0.5000

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93	15	2	250112.7220	250112.6925	0.0295	0.5000
94	15	1	250111.4100	250111.5664	-0.1564	0.7000
95	15	0	250111.2750	250111.1910	0.0840	0.7000
96	26	0	421662.9010	421662.8171	0.0839	0.2000
97	26	1	421663.6200	421663.4471	0.1729	0.2000
98	26	2	421665.4650	421665.3373	0.1277	0.2000
99	26	3	421668.6210	421668.4879	0.1331	0.2000
100	26	4	421673.0240	421672.8990	0.1250	0.2000
101	26	5	421678.7030	421678.5712	0.1318	0.2000
102	26	6	421685.6360	421685.5048	0.1312	0.2000
103	26	7	421693.8320	421693.7007	0.1313	0.2000
104	26	8	421703.2870	421703.1593	0.1277	0.2000
105	26	9	421714.0120	421713.8818	0.1302	0.2000
106	26	10	421725.9910	421725.8689	0.1221	0.2000
107	26	11	421739.2540	421739.1217	0.1323	0.2000
108	26	12	421753.7710	421753.6416	0.1294	0.2000
109	26	18	421867.5920	421867.4475	0.1445	0.2000
110	26	21	421941.7500	421941.5853	0.1647	0.2000
111	26	24	422027.4910	422027.2896	0.2014	0.2000
112	43	2	685503.9400	685504.0284	-0.0884	0.2000
113	43	4	685516.0300	685516.1818	-0.1518	0.2000
114	43	5	685525.2000	685525.2982	-0.0982	0.2000
115	43	6	685536.2200	685536.4422	-0.2222	0.2000
116	43	12	685645.5500	685645.9549	-0.4049	0.2000
117	43	18	685828.7600	685828.8750	-0.1150	0.2000
118	43	24	686085.4300	686085.8005	-0.3705	0.2000
119	43	30	686417.7100	686417.5691	0.1409	0.2000
120	43	36	686826.2500	686825.2574	0.9926	0.2000
121	43	42	687311.0700	687310.1815	0.8885	0.2000
122	44	0	700954.5700	700955.2607	-0.6907	0.2000
123	44	1	700955.4700	700956.2953	-0.8253	0.2000
124	44	2	700958.9900	700959.3991	-0.4091	0.2000
125	44	4	700971.9500	700971.8159	0.1341	0.2000
126	44	5	700980.9200	700981.1299	-0.2099	0.2000
127	44	6	700992.5400	700992.5155	0.0245	0.2000
128	44	7	701005.8400	701005.9736	-0.1336	0.2000
129	44	9	701038.9700	701039.1126	-0.1426	0.2000
130	44	12	701103.9600	701104.4021	-0.4421	0.7000
131	44	15	701188.2000	701188.4376	-0.2376	0.8000
132	44	18	701291.4000	701291.2878	0.1122	0.9000
133	44	21	701412.4400	701413.0369	-0.5969	0.2000
134	44	24	701553.2100	701553.7842	-0.5742	0.2000
135	44	27	701713.7000	701713.6446	0.0554	0.2000
136	44	30	701892.5000	701892.7480	-0.2480	0.2000
137	44	33	702091.0700	702091.2397	-0.1697	0.2000
138	44	36	702309.1400	702309.2803	-0.1403	0.2000
139	44	39	702546.9600	702547.0457	-0.0857	0.2000
140	44	42	702804.9500	702804.7271	0.2229	0.2000
141	46	2	731844.9600	731845.0438	-0.0838	0.2000
142	46	4	731857.7200	731857.9848	-0.2648	0.2000
143	46	5	731867.3100	731867.6922	-0.3822	0.2000
144	46	6	731879.0900	731879.5585	-0.4685	0.2000
145	46	12	731995.6700	731996.1696	-0.4996	0.2000
146	46	18	732190.8800	732190.9474	-0.0674	0.2000
147	46	24	732464.3400	732464.5310	-0.1910	0.2000
148	46	30	732817.5500	732817.8149	-0.2649	0.2000
149	46	36	733251.6400	733251.9493	-0.3093	0.2000
150	46	42	733768.0300	733768.3400	-0.3100	0.2000
151	67	0	1053783.5100	1053782.5530	0.9570	0.2000

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152	67	1	1053784.6010	1053784.0693	0.5317	0.2000
153	67	2	1053789.3900	1053788.6186	0.7714	0.2000
154	67	4	1053807.3300	1053806.8179	0.5121	0.2000
155	67	5	1053820.5200	1053820.4696	0.0504	0.2000
156	67	6	1053837.9300	1053837.1576	0.7724	0.2000
157	67	12	1054001.4100	1054001.1564	0.2536	0.2000
158	67	18	1054275.3400	1054275.1040	0.2360	0.2000
159	67	27	1054894.5800	1054894.3031	0.2769	0.2000
160	67	36	1055767.8500	1055767.7342	0.1158	0.2000
161	67	45	1056902.0800	1056901.9497	0.1303	0.2000
162	67	54	1058304.0300	1058305.3742	-1.3442	0.3000
163	67	63	1059988.3300	1059988.3042	0.0258	0.2000
164	80	0	1250478.4800	1250479.5994	-1.1194	0.3000
165	80	1	1250480.7200	1250481.3640	-0.6440	0.2000
166	80	2	1250486.5600	1250486.6578	-0.0978	0.2000
167	80	15	1250876.3200	1250877.3399	-1.0199	0.2000
168	80	24	1251500.4100	1251500.6783	-0.2683	0.3000
169	80	33	1252418.4200	1252417.9885	0.4315	0.2000
170	80	42	1253637.0500	1253636.3321	0.7179	0.2000
171	80	51	1255164.6600	1255165.0010	-0.3410	0.2000
172	80	60	1257014.3700	1257015.5168	-1.1468	0.3000
173	80	69	1259200.1800	1259201.6314	-1.4514	0.3000
174	80	78	1261740.1700	1261739.3265	0.8435	0.2000
175	81	75	1275995.3900	1275996.4071	-1.0171	0.2000
176	81	78	1276892.3100	1276891.7560	0.5540	0.2000
177	82	18	1281119.1800	1281120.2762	-1.0962	0.3000
178	82	24	1281577.3700	1281577.3894	-0.0194	0.2000
179	82	36	1282894.1500	1282893.5829	0.5671	0.2000
180	82	39	1283309.3000	1283307.9790	1.3210	0.3000
181	82	45	1284242.1800	1284241.5580	0.6220	0.3000

Sigma=0.382230 181 Transitions in fit, Sigma. w = 1.627328 175 Degrees of freedom.

Table 2. Correlation Coefficients for PF₃ in ground state

	B	DJ	DJK	HJ	HJK	HKJ
B	1.0000					
DJ	0.8617	1.0000				
DJK	0.0493	-0.2802	1.0000			
HJ	0.7394	0.9668	-0.3823	1.0000		
HJK	-0.0024	-0.2907	0.8267	-0.4470	1.0000	
HKJ	0.0529	0.1317	-0.1767	0.2559	-0.6838	1.0000

Spectrum in the State $v_2 = 1$

This state shows the characteristic intensity pattern of non-degenerate state in its k structure. The population of the four fundamental vibrations of PF₃ are given in the Table 3. This Table shows the $v_2=1$ state has enough population (9.5%) relative to ground state to observe the signals. The $v_2=1$ state was assigned by Hirota and Morino¹ to the intense vibrational satellite to low frequency of the ground state. Their assignment was based on intensity arguments and the absence of l-doublets.

The frequencies of Refs 5 and 7 were mixed together in order to obtain improved constants. The quartic constants were obtained with good agreement with previous work. It should be noticed that the distortion constants obtained are not very different from those of the ground state. H_J , H_{Jk} , H_{kJ} , H_k centrifugal distortions were obtained with new values and higher accuracy. For PF₃, $H_{Jk}<0$ while both H_J and $H_{kJ}>0$. This behavior is typical of an oblate top. The results of refinements are listed in Table 4 and obtained parameters are shown in Table 5.

Table 3. Approximate populations of the fundamental vibrational states at 298 K.

Sym. Species	N ₀	Type of mode	Frequency /cm ⁻¹	Percentage population relative to G.S.*
A ₁	1	Sym str	892	1.35
A ₂	2	Sym deform	487	9.5
E	3	Deg str	860	1.6
E	4	Deg deform	344	19

* These figures do not include a degeneracy factor.

Table 4. Results of Refinement of Observed Frequencies for PF₃ in $\nu_2 = 1$ State

S. No.	J	K	Fobs/MHz	Calc/MHz	(Obs-Calc)/MHz	Error/MHz
1	0	0	15622.2700	15622.2914	-0.0214	0.0500
2	1	1	31244.4410	31244.4435	-0.0025	0.1000
3	1	0	31244.4410	31244.3976	0.0434	0.1000
4	6	6	109351.5000	109351.4473	0.0527	0.1000
5	6	5	109349.6870	109349.6828	0.0042	0.1000
6	6	4	109348.1870	109348.2393	-0.0523	0.1000
7	6	3	109347.0620	109347.1167	-0.0547	0.1000
8	6	2	109346.3120	109346.3149	-0.0029	0.1000
9	6	1	109345.6870	109345.8339	-0.1469	0.2000
10	6	0	109345.6870	109345.6736	0.0134	0.2000
11	7	7	124971.8120	124971.7634	0.0486	0.2000
12	7	6	124969.4370	124969.3801	0.0569	0.1000
13	7	5	124967.3750	124967.3638	0.0112	0.1000
14	7	4	124965.7500	124965.7144	0.0356	0.1000
15	7	3	124964.5000	124964.4316	0.0684	0.1000
16	7	2	124963.4370	124963.5154	-0.0784	0.1000
17	7	1	124962.9370	124962.9658	-0.0288	0.1000
18	7	0	124962.9370	124962.7825	0.1545	0.1000
19	8	7	140588.5680	140588.5130	0.0550	0.3000
20	8	6	140585.8820	140585.8323	0.0497	0.3000
21	8	5	140583.5860	140583.5644	0.0216	0.3000
22	8	4	140581.6780	140581.7091	-0.0311	0.3000
23	8	3	140580.2160	140580.2662	-0.0502	0.3000
24	8	2	140579.1940	140579.2357	-0.0417	0.3000
25	8	0	140578.4160	140578.4113	0.0047	0.3000
26	10	9	171824.8750	171824.8952	-0.0202	0.3000
27	10	8	171820.5620	171820.6106	-0.0486	0.3000
28	10	7	171816.8120	171816.8309	-0.0189	0.3000
29	10	6	171813.5620	171813.5558	0.0062	0.3000
30	10	5	171810.8120	171810.7850	0.0270	0.3000
31	10	4	171808.5620	171808.5183	0.0437	0.3000
32	10	3	171806.8120	171806.7555	0.0565	0.3000
33	10	2	171805.5620	171805.4964	0.0656	0.3000
34	10	1	171804.7500	171804.7410	0.0090	0.5000
35	10	0	171804.7500	171804.4893	0.2607	0.5000
36	13	0	218627.9130	218627.8888	0.0242	0.2000
37	13	1	218628.1860	218628.2090	-0.0230	0.2000
38	13	2	218629.1730	218629.1697	0.0033	0.2000
39	13	3	218630.7650	218630.7709	-0.0059	0.2000
40	13	4	218633.0180	218633.0128	0.0052	0.2000
41	13	5	218635.9060	218635.8955	0.0105	0.2000
42	13	6	218639.4280	218639.4194	0.0086	0.2000
43	13	7	218643.6020	218643.5846	0.0174	0.2000
44	13	8	218648.4190	218648.3915	0.0275	0.2000

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45	13	9	218653.8790	218653.8405	0.0385	0.2000
46	13	10	218659.9680	218659.9321	0.0359	0.2000
47	13	11	218666.7270	218666.6667	0.0603	0.2000
48	13	12	218674.1040	218674.0450	0.0590	0.2000
49	13	13	218682.1340	218682.0674	0.0666	0.2000
50	14	10	234265.0000	234265.0821	-0.0821	0.4000
51	14	9	234258.5620	234258.5572	0.0048	0.4000
52	14	8	234252.6870	234252.7207	-0.0337	0.4000
53	14	7	234247.6250	234247.5719	0.0531	0.4000
54	14	6	234243.1250	234243.1105	0.0145	0.4000
55	14	5	234239.2500	234239.3360	-0.0860	0.4000
56	14	4	234236.1870	234236.2482	-0.0612	0.4000
57	14	3	234233.8120	234233.8469	-0.0349	0.4000
58	14	2	234232.1250	234232.1318	-0.0068	0.4000
59	14	1	234230.8750	234231.1028	-0.2278	0.6000
60	14	0	234230.8750	234230.7598	0.1152	0.6000
61	17	0	281021.9740	281022.0098	-0.0358	0.2000
62	17	1	281022.3980	281022.4210	-0.0230	0.2000
63	17	2	281023.6260	281023.6545	-0.0285	0.2000
64	17	3	281025.6830	281025.7106	-0.0276	0.2000
65	17	4	281028.5610	281028.5894	-0.0284	0.2000
66	17	5	281032.2630	281032.2911	-0.0281	0.2000
67	17	6	281036.7950	281036.8159	-0.0209	0.2000
68	17	7	281042.1530	281042.1644	-0.0114	0.2000
69	17	8	281048.3400	281048.3369	0.0031	0.2000
70	17	9	281055.3370	281055.3338	0.0032	0.2000
71	17	10	281063.1610	281063.1559	0.0051	0.2000
72	17	11	281071.7870	281071.8037	-0.0167	0.2000
73	17	12	281081.3020	281081.2779	0.0241	0.2000
74	17	13	281091.6180	281091.5793	0.0387	0.2000
75	17	14	281102.7560	281102.7087	0.0473	0.2000
76	17	15	281114.7330	281114.6671	0.0659	0.2000
77	17	16	281127.5300	281127.4554	0.0746	0.2000
78	17	17	281141.1690	281141.0746	0.0944	0.2000
79	22	0	358938.4140	358938.5353	-0.1213	0.2000
80	22	1	358938.9860	358939.0597	-0.0737	0.2000
81	22	2	358940.5320	358940.6327	-0.1007	0.2000
82	22	3	358943.1590	358943.2546	-0.0956	0.2000
83	22	4	358946.8300	358946.9255	-0.0955	0.2000
84	22	5	358951.5410	358951.6457	-0.1047	0.2000
85	22	6	358957.3270	358957.4157	-0.0887	0.2000
86	22	7	358964.1570	358964.2358	-0.0788	0.2000
87	22	8	358972.0270	358972.1068	-0.0798	0.2000
88	22	9	358980.9600	358981.0291	-0.0691	0.2000
89	22	10	358990.9440	358991.0035	-0.0595	0.2000
90	22	11	359001.9770	359002.0309	-0.0539	0.2000
91	22	12	359014.0640	359014.1121	-0.0481	0.2000
92	22	13	359027.2080	359027.2482	-0.0402	0.2000
93	22	14	359041.4110	359041.4401	-0.0291	0.2000
94	22	15	359056.6790	359056.6891	-0.0101	0.2000
95	22	16	359073.0000	359072.9964	0.0036	0.2000
96	22	17	359090.3810	359090.3633	0.0177	0.2000
97	22	18	359108.8260	359108.7913	0.0347	0.2000
98	22	19	359128.3390	359128.2817	0.0573	0.2000
99	22	20	359148.9130	359148.8363	0.0767	0.2000
100	22	21	359170.5610	359170.4567	0.1043	0.2000
101	22	22	359193.2660	359193.1447	0.1213	0.2000
102	43	0	684767.5220	684767.7457	-0.2237	0.2000
103	43	1	684768.3420	684768.7347	-0.3927	0.2000

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104	43	2	684771.7440	684771.7016	0.0424	0.2000
105	43	4	684783.5030	684783.5707	-0.0677	0.2000
106	43	5	684792.2940	684792.4738	-0.1798	0.2000
107	43	12	684910.4200	684910.2964	0.1236	0.2000
108	43	15	684991.0200	684990.6056	0.4144	0.2000
109	43	21	685205.8200	685205.2015	0.6185	0.2000
110	43	24	685340.1800	685339.6475	0.5325	0.2000
111	43	27	685492.7500	685492.3205	0.4295	0.2000
112	43	30	685662.7500	685663.3333	-0.5833	0.2000
113	43	33	685851.9500	685852.8120	-0.8620	0.2000
114	43	36	686060.1600	686060.8960	-0.7360	0.2000
115	43	39	686287.3900	686287.7379	-0.3479	0.2000
116	44	0	700208.4700	700208.4168	0.0532	0.2000
117	44	1	700209.4400	700209.4273	0.0127	0.2000
118	44	2	700212.4800	700212.4590	0.0210	0.2000
119	44	4	700224.6000	700224.5869	0.0131	0.2000
120	44	5	700233.8400	700233.6841	0.1559	0.2000
121	44	6	700244.9200	700244.8044	0.1156	0.2000
122	44	9	700290.4600	700290.3144	0.1456	0.2000
123	44	12	700354.3000	700354.0759	0.2241	0.2000
124	44	15	700435.7300	700436.1364	-0.4064	0.2000
125	44	18	700536.6900	700536.5571	0.1329	0.2000
126	44	21	700655.6500	700655.4125	0.2375	0.2000
127	44	24	700792.8500	700792.7909	0.0591	0.2000
128	44	27	700948.7500	700948.7941	-0.0441	0.2000
129	44	30	701122.9960	701123.5375	-0.5415	0.2000
130	44	33	701317.2300	701317.1501	0.0799	0.2000
131	44	36	701530.5000	701529.7744	0.7256	0.2000
132	44	39	701761.7900	701761.5665	0.2235	0.2000
133	44	42	702013.1600	702012.6961	0.4639	0.2000
134	49	2	777290.2120	777290.1098	0.1022	0.2000
135	49	4	777303.0950	777303.5203	-0.4253	0.2000

Sigma=0.198847, 135 Transitions in fit, Sigma w=995437, 129 Degrees of freedom

Table 5. Results of refinement of observed frequencies for PF₃ in ground and $v_2 = 1$ state.

Parameter	G.S. (Ref. 6)	G.S. this work	$v_2 = 1$ (Ref. 6)	$v_2 = 1$ (this work)
C_v /MHz	4785.965*	4785.965*	4785.965*	4785.965*
B_v /MHz	7819.99520 (11)	7819.9907 (13)	7811.16319 (13)	7811.1611(12)
D_J /kHz	7.85185 (14)	7.84984 (41)	7.71931 (20)	7.7139 (14)
D_{JK} /kHz	-11.76828 (54)	-11.7644 (11)	-11.47187 (48)	-11.4586 (62)
H_J /mHz	16.254 (79)	15.678 (36)	15.731 (98)	14.13 (39)
H_{JK} /mHz	-69.88 (63)	-66.46 (12)	-61.22 (64)	-56.9 (16)
H_{KJ} /mHz	93.0 (14)	87.42 (15)	80.05 (16)	77.5 (16)

* constrained at this value.

Spectrum in the state $v_4 = 1$

As Table 3 shows, this state has enough population relative to the ground state to show strong signals in its spectrum. The theory for the rotational spectrum of an E degenerate vibrational state of a C_{3v} molecule is well known¹³. Essentially the two components of the vibration each give rise to a series of k levels which are coupled to each other by l-resonance. This results in two series of transitions which are best labeled by the pseudo-quantum number kl -1. The l-resonance splitting is greatest for levels with low values of this label. Perturbation theory yields the approximate frequency expression

$$v = \frac{(q_t^+)^2(J+1)[(J+1)^2 - (kl-1)^2]}{4(B-C+C\zeta_t)(kl-1)} \quad \text{when } (kl-1) \neq 0 \quad (2)$$

where q_t^+ is the l-type doubling constant, B and C are rotational constants, and ζ_t is the z-coriolis constant for the vibrational state v_t . The degree of l-resonance thus largely depends on the ratio of q_t^+ to the resonance denominator $(B-C+C\zeta_t)$. With low to moderate values of this denominator, the spectrum usually found consists of two extreme outer lines for $kl-1=0$ (the l-doublets) and a center group of lines for $kl-1 \neq 0$ whose structure depends very strongly on other parameters such as the centrifugal distortion constants. As the strength of the resonance increases, the lines of the center group spread out until the low $(kl-1)$ transitions approach the positions of the l-doublets.

In order to obtain more accuracy in rotational energies for singly excited vibrational states than can be obtained from perturbation theory, it is necessary to set up a rotational Hamiltonian as a matrix (H) in equation $H\psi = E\psi$ and diagonalise to obtain the energy¹⁴⁻²². The Hamiltonian was set up for a symmetric top molecule like PF_3 . This rotation-vibrational Hamiltonian has two different blocks that belong to the different $l = +1$ and $l = -1$ series. k and l are no longer good quantum numbers, but $(k-l)$ or $(kl-1)$ may be used to distinguish between the symmetry species. Those levels with $(kl-1) = 3n$, where n is an integer, are of species A_1 or A_2 . If $(kl-1) \neq 3n$ the species are E. The q_t^+ produces a first order splitting of the $(kl-1) = 0$, A_1A_2 pair, which are the familiar l-doublets, as shown by Grenier-Besson and Amat¹³. The main difference from the ground state spectra is the splitting of the $|k-l| = 0$ into two widely separate l-doublets and the splitting due to l-resonance.

The diagonal matrix elements are given by:

$$\begin{aligned} \langle v_t, l_t, J, k | H/h | v_t, l_t, J, k \rangle = & BJ(J+1) + (C-B)k^2 - 2C\zeta_k l - D_J J^2(J+1)^2 \\ & - D_{Jk} J(J+1)k^2 - D_k k^4 + \eta_J J(J+1)kl + \eta_k k^3 l \\ & + H_J J^3(J+1)^3 + H_{Jk} J^2(J+1)^2 k^2 + H_{kJ} J(J+1)k^4 + H_k k^6 \end{aligned} \quad (3)$$

In addition, there are off-diagonal terms that arise from the transformation. The major one of these gives rise to the l doubling:

$$\begin{aligned} & \langle v_t, l, J, k | H/h | v_t, l \pm 2, J, k \pm 2 \rangle \\ = & -\frac{1}{4} q_t^+ \{ (v_t \mp 1)(v_t \pm 1 + 2)[J(J+1) - k(k \pm 1)] [J(J+1) - (k \pm 1)(k \pm 2)] \}^{1/2} \end{aligned} \quad (4)$$

$$\begin{aligned} \text{and } \langle v_t, l, J, k | H/h | v_t, l \pm 2, J, k \mp 1 \rangle = & -r_t [(v_t+1)^2 - (l \pm 1)^2]^{1/2} [J(J+1) \\ & - k(k \mp 1)]^{1/2} (2k \mp 1) \end{aligned} \quad (5)$$

and hence, the lines can be assigned.

The frequencies of Refs 4 and 6 were mixed together in order to improve the accuracy of the parameters in this state, then a weighted least-squares method¹² was used to fit these frequencies to equation 3, in which the weights were taken to be $w = 1/(\text{observed error})^2 = 1/(0.1)^2$, where 0.1 in MHz is estimated uncertainty in an observation for each unblended line. Some of the lines have uncertainty between 0.2 to 0.5 MHz due to overlapping or blending lines. The fit to the transitions are given in Tables 6,7 and the constants obtained are given in Table 8.

Table 6. Results of Refinement of Observed Frequencies for PF₃ in $\nu_4 = 1$ State

S. No.	J	K 1-1	K	l	sym	Fobs/MHz	(Obs-Calc)/MHz	Error/MHz
1	0	-1	0,	1	E	15646.1620	0.0018	0.0020
2	1	0	1,	1	A+	31350.8700	-0.1583	0.1000
3	1	-1	0,	1	E	31328.9800	0.0043	0.1000
4	1	-2	1,-	1	E	31292.3000	-0.0086	0.1000
5	-1	0	-1,-	1	A-	31233.0900	0.0244	0.1000
6	6	0	1,	1	A+	109718.4400	-0.0400	0.1000
7	6	-1	0,	1	E	109718.0480	-0.0753	0.1000
8	6	-2	1,-	1	E	109716.7040	-0.0811	0.1000
9	6	-3	2,-	1	A+	109713.3440	-0.1208	0.1000
10	6	-4	3,-	1	E	109705.0400	-0.0346	0.1000
11	6	-5	4,-	1	E	109683.1600	0.0013	0.1000
12	6	-6	5,-	1	A+	109626.1520	-0.0431	0.1000
13	6	-7	6,-	1	E	109521.2400	-0.0129	0.1000
14	6	5	6,	1	E	109349.6800	0.1111	0.1000
15	6	4	5,	1	E	109324.6480	0.0264	0.1000
16	6	3	4,	1	A+	109313.8740	-0.0716	0.1000
17	6	2	3,	1	E	109309.0020	0.1343	0.1000
18	6	1	2,	1	E	109306.5710	0.0478	0.1000
19	-6	0	-1,-	1	A-	109305.8670	0.0385	0.1000
20	7	0	1,	1	A+	125388.6090	-0.0857	0.1000
21	7	-2	1,-	1	E	125387.9390	-0.0049	0.1000
22	7	-3	2,-	1	A+	125386.4510	-0.0182	0.1000
23	7	-4	3,-	1	E	125382.6500	-0.0019	0.1000
24	7	-5	4,-	1	E	125373.3000	0.0142	0.1000
25	7	-6	5,-	1	A+	125348.7060	-0.0244	0.1000
26	7	-7	6,-	1	E	125284.9820	0.0056	0.1000
27	7	-8	7,-	1	E	125166.3260	-0.0308	0.1000
28	7	6	7,	1	A+	124970.9930	0.0003	0.1000
29	7	4	5,	1	E	124929.3600	-0.0136	0.1000
30	7	3	4,	1	A+	124922.9000	-0.0702	0.1000
31	7	2	3,	1	E	124919.4530	-0.0072	0.1000
32	7	1	2,	1	E	124917.7170	0.0011	0.1000
33	-7	0	-1,-	1	A-	124917.1650	-0.0111	0.1000
34	8	0	1,	1	A+	141057.2880	-0.0805	0.5000
35	8	-3	2,-	1	A+	141056.6400	-0.1209	0.5000
36	8	-3	2,-	1	A+	141056.6400	-0.1209	0.3000
37	8	-4	3,-	1	E	141055.1280	-0.0251	0.3000
38	8	-5	4,-	1	E	141051.0960	-0.0557	0.3000
39	8	-6	5,-	1	A+	141040.9150	0.0184	0.3000
40	8	-7	6,-	1	E	141013.7500	-0.0510	0.3000
41	8	-8	7,-	1	E	140943.3120	-0.0122	0.3000
42	8	-9	8,-	1	A+	140811.0190	-0.1045	0.3000
43	8	7	8,	1	E	140591.6140	-0.1756	0.3000
44	8	6	7,	1	A+	140559.0770	0.0105	0.3000
45	8	5	6,	1	E	140543.9860	-0.0635	0.3000
46	8	4	5,	1	E	140536.0940	-0.0579	0.3000
47	8	3	4,	1	A+	140531.5150	-0.1528	0.4000
48	8	2	3,	1	E	140528.8300	-0.0765	0.3000
49	8	1	2,	1	E	140527.4680	-0.0069	0.3000
50	-8	0	-1,-	1	A-	140526.9570	-0.0592	0.3000
51	-9	0	-1,-	1	A-	156135.1570	-0.0038	0.0500

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52	9	-1	0, 1	E	156724.4070	0.0270	0.2000
53	9	-2	1, -1	E	156724.4070	-0.1228	0.2000
54	9	-3	2, -1	A+	156724.4070	-0.3509	0.2000
55	9	-3	2, -1	A+	156724.8120	0.0541	0.2000
56	9	-4	3, -1	E	156724.4070	0.0338	0.2000
57	9	-5	4, -1	E	156723.0060	0.0093	0.0500
58	9	-6	5, -1	A+	156718.8750	-0.0011	0.0500
59	9	-7	6, -1	E	156707.8670	0.0243	0.0500
60	9	-8	7, -1	E	156678.2710	-0.0327	0.0500
61	9	-9	8, -1	A+	156601.1750	-0.0093	0.0500
62	9	-10	9, -1	E	156455.4580	-0.0479	0.0500
63	9	0	1, 1	A+	156724.4070	0.0979	0.2000
64	9	1	2, 1	E	156135.5530	-0.0262	0.0500
65	9	2	3, 1	E	156136.8290	-0.0139	0.0500
66	9	3	4, 1	A+	156139.1120	-0.1292	0.2000
67	9	4	5, 1	E	156142.7330	-0.0479	0.2000
68	9	5	6, 1	E	156148.4460	-0.0395	0.0500
69	9	6	7, 1	A+	156157.8900	-0.0059	0.0500
70	9	7	8, 1	E	156175.1720	-0.0086	0.0500
71	9	8	9, 1	E	156211.9380	0.0052	0.0500
72	-10	0	-1, -1	A-	171741.4590	0.0368	0.2000
73	10	1	2, 1	E	171741.9290	0.1028	0.2000
74	10	2	3, 1	E	171743.0950	0.0958	0.2000
75	10	3	4, 1	A+	171745.2700	0.0331	0.2000
76	10	4	5, 1	E	171748.3240	0.0394	0.2000
77	10	5	6, 1	E	171752.9870	0.0465	0.2000
78	10	6	7, 1	A+	171759.8690	0.0031	0.2000
79	10	7	8, 1	E	171770.8480	-0.0225	0.2000
80	10	8	9, 1	E	171790.5970	0.0865	0.2000
81	10	9	10, 1	A+	171831.3830	-0.0044	0.2000
82	10	-7	6, -1	E	172385.6760	-0.0975	0.2000
83	10	-8	7, -1	E	172374.0480	-0.0179	0.2000
84	10	-9	8, -1	A+	172342.0350	-0.1442	0.2000
85	11	-9	8, -1	A+	188039.4240	-0.0872	0.3000
86	11	9	10, 1	A+	187405.0560	0.0391	0.3000
87	11	8	9, 1	E	187382.9950	0.0642	0.3000
88	11	7	8, 1	E	187370.2270	-0.0177	0.3000
89	11	6	7, 1	A+	187361.9080	-0.1072	0.3000
90	11	5	6, 1	E	187356.2500	-0.0182	0.3000
91	11	4	5, 1	E	187352.0450	-0.0799	0.3000
92	11	2	3, 1	E	187347.1100	-0.0351	0.3000
93	-11	0	-1, -1	A-	187345.5800	-0.0329	0.3000
94	13	4	5, 1	E	218553.6300	0.1727	0.3000
95	13	5	6, 1	E	218557.4500	0.1656	0.3000
96	13	6	7, 1	A+	218562.3800	0.1645	0.3000
97	13	7	8, 1	E	218568.6000	0.0797	0.3000
98	13	9	10, 1	A+	218587.5800	-0.2318	0.3000
99	13	-12	11, -1	A+	219329.2200	-0.2802	0.3000
100	-14	0	-1, -1	A-	234144.0200	0.1279	0.4000
101	14	-1	0, 1	E	235026.3200	-0.3015	0.5000
102	14	-2	1, -1	E	235027.2060	-0.0199	0.4000
103	14	-3	2, -1	A+	235028.4960	-0.9200	0.4000
104	14	-3	2, -1	A+	235029.3400	-0.0760	0.4000
105	14	-4	3, -1	E	235031.0900	-0.1132	0.4000

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106	14	-5	4, -1	E	235033.6300	-0.2196	0.4000
107	14	-6	5, -1	A+	235036.7500	-0.1652	0.4000
108	14	-7	6, -1	E	235039.8960	-0.3406	0.4000
109	14	-9	8, -1	A+	235045.8900	-0.3331	0.4000
110	14	-10	9, -1	E	235047.2460	0.0165	0.0500
111	14	-11	10, -1	E	235044.0710	-0.0054	0.0500
112	14	-12	11, -1	A+	235030.4000	-0.2592	0.4000
113	14	-13	12, -1	E	234990.2920	-0.0408	0.0500
114	14	-14	13, -1	E	234881.2940	-0.0921	0.0500
115	14	-15	14, -1	A+	234669.8610	-0.1393	0.0500
116	14	0	1, 1	A+	235026.3200	0.0220	0.4000
117	14	2	3, 1	E	234145.6300	0.1754	0.4000
118	14	3	4, 1	A+	234147.2640	-0.6124	0.4000
119	14	3	4, 1	A+	234148.0300	0.1536	0.4000
120	14	4	5, 1	E	234150.4800	0.0493	0.4000
121	14	5	6, 1	E	234154.4200	0.1504	0.4000
122	14	6	7, 1	A+	234159.2400	0.1127	0.4000
123	14	7	8, 1	E	234165.0000	-0.1690	0.4000
124	14	8	9, 1	E	234172.6090	-0.0777	0.0500
125	14	9	10, 1	A+	234182.0400	-0.1894	0.4000
126	14	10	11, 1	E	234194.9000	-0.0076	0.0500
127	14	11	12, 1	E	234213.0500	-0.1365	0.4000
128	14	12	13, 1	A+	234243.0960	-0.0747	0.0500
129	14	13	14, 1	E	234301.4300	-0.0759	0.0500
130	-19	0	-1, -1	A-	312082.2740	0.0074	0.0500
131	19	-1	0, 1	E	313256.7500	0.0518	0.0500
132	19	-2	1, -1	E	313257.6710	0.0098	0.0500
133	19	-3	2, -1	A+	313260.9910	0.0513	0.0500
134	19	-4	3, -1	E	313263.6050	0.0662	0.0500
135	19	-5	4, -1	E	313267.7930	0.0738	0.0500
136	19	-6	5, -1	A+	313272.7750	-0.0067	0.0500
137	19	-7	6, -1	E	313278.7630	0.0545	0.0500
138	19	-8	7, -1	E	313285.4880	0.0234	0.0500
139	19	-9	8, -1	A+	313292.9840	-0.0107	0.0500
140	19	-10	9, -1	E	313301.1840	-0.0284	0.0500
141	19	-11	10, -1	E	313309.9210	-0.0588	0.0500
142	19	-12	11, -1	A+	313319.0110	-0.0559	0.0500
143	19	-13	12, -1	E	313328.0700	-0.0022	0.0500
144	19	-14	13, -1	E	313336.2560	0.0066	0.0500
145	19	-15	14, -1	A+	313342.1950	0.0908	0.0500
146	19	-16	15, -1	E	313342.1950	-0.1566	0.0500
147	19	-17	16, -1	E	313328.9490	0.0039	0.0500
148	19	-18	17, -1	A+	313280.2910	0.1083	0.0500
149	19	-19	18, -1	E	313141.9250	0.0523	0.0500
150	19	-20	19, -1	E	312867.7530	-0.0153	0.0500
151	19	0	1, 1	A+	313256.2710	0.0563	0.0500
152	19	1	2, 1	E	312082.9560	0.0601	0.0500
153	19	2	3, 1	E	312083.9570	0.0397	0.0500
154	19	3	4, 1	A+	312087.4220	0.1422	0.0500
155	19	4	5, 1	E	312089.8380	-0.0187	0.0500
156	19	5	6, 1	E	312094.3230	0.0029	0.0500
157	19	6	7, 1	A+	312099.8580	0.0528	0.0500
158	19	7	8, 1	E	312106.3880	0.0498	0.0500
159	19	8	9, 1	E	312113.9480	-0.0088	0.0500
160	19	9	10, 1	A+	312122.6510	-0.0667	0.0500
161	19	10	11, 1	E	312132.6390	-0.0689	0.0500
162	19	11	12, 1	E	312144.0050	-0.0613	0.0500
163	19	12	13, 1	A+	312157.0120	-0.0114	0.0500

Contd...

164	19	13	14, 1	E	312172.0020	0.0205	0.0500
165	19	14	15, 1	E	312189.6500	-0.0375	0.0500
166	19	15	16, 1	A+	312211.6130	-0.0234	0.0500
167	19	16	17, 1	E	312241.1290	0.0151	0.0500
168	19	17	18, 1	E	312286.1860	0.0186	0.0500
169	19	18	19, 1	A+	312368.5640	0.0643	0.0500
170	-32	0	-1, -1	A-	514236.2660	0.0117	0.0500
171	32	-1	0, 1	E	516146.7440	-0.2492	0.5000
172	32	-2	1, -1	E	516149.4920	0.0416	0.2000
173	32	-3	2, -1	A+	516144.3940	-0.0970	0.0500
174	32	-4	3, -1	E	516155.5970	-0.0531	0.0500
175	32	-5	4, -1	E	516164.7740	0.1003	0.0500
176	32	-6	5, -1	A+	516173.8690	0.0981	0.0500
177	32	-7	6, -1	E	516184.3260	0.0913	0.0500
178	32	-12	11, -1	A+	516259.8010	0.0455	0.0500
179	32	-15	14, -1	A+	516323.8580	0.0138	0.0500
180	32	-18	17, -1	A+	516401.7980	0.0248	0.0500
181	32	-21	20, -1	A+	516492.9300	0.0848	0.0500
182	32	0	1, 1	A+	516146.7440	0.5797	0.5000
183	32	1	2, 1	E	514227.5060	0.5029	0.5000
184	32	2	3, 1	E	514227.5060	-0.0367	0.5000
185	32	5	6, 1	E	514243.3190	-0.0074	0.0500
186	32	6	7, 1	A+	514251.7950	-0.0053	0.0500
187	32	9	10, 1	A+	514286.5670	-0.0072	0.0500
188	32	12	13, 1	A+	514335.4100	-0.0002	0.0500
189	32	15	16, 1	A+	514398.4890	0.0224	0.0500
190	32	18	19, 1	A+	514476.1650	0.0767	0.0500
191	35	-3	2, -1	A+	562841.9280	-0.3244	0.0500
192	35	1	2, 1	E	560750.9490	0.0336	0.0500
193	-37	0	-1, -1	A-	591715.6670	-0.0926	0.1500
194	37	-2	1, -1	E	593924.5670	0.2571	0.1500
195	37	-4	3, -1	E	593863.9510	0.0717	0.0500
196	37	-5	4, -1	E	593939.4300	0.1036	0.1000
197	37	-6	5, -1	A+	593951.2990	0.1359	0.0500
198	37	-16	15, -1	E	594153.1230	-0.0780	0.5000
199	37	-21	20, -1	A+	594321.7720	-0.1055	0.0500
200	37	-27	26, -1	A+	594581.2910	-0.1826	0.0500
201	37	-30	29, -1	A+	594729.6500	0.1751	0.0500
202	37	-36	35, -1	A+	594849.3550	-0.0390	0.0500
203	37	-38	37, -1	E	594153.1230	0.0304	0.0500
204	37	0	1, 1	A+	593920.0380	-0.5038	0.1500
205	37	2	3, 1	E	591722.3810	0.0613	0.0500
206	37	4	5, 1	E	591730.5680	-0.1513	0.0500
207	37	15	16, 1	A+	591915.1950	-0.0252	0.0500
208	37	24	25, 1	A+	592229.7810	0.0203	0.0500
209	37	30	31, 1	A+	592532.9040	-0.0016	0.0500
210	37	33	34, 1	A+	592736.3800	-0.0005	0.0500
211	37	36	37, 1	A+	593136.0440	-0.0226	0.0500
212	55	-5	4, -1	E	872283.3560	-0.3609	0.1500
213	55	-2	1, -1	E	872259.7350	0.0618	0.0500
214	55	-1	0, 1	E	872255.6810	0.0300	0.1000
215	55	0	1, 1	A+	872254.2250	-0.0524	0.1000

Sigma = .144795, 215 Transitions in fit, Sigma.w = 1.111612, 202 Degrees of freedom

Table 7. Correlation coefficients of PF₃ for the $v_4 = 1$ state.

	B	DJ	DJK	HJ	HJK	Azeta	nJ	nK	qv	qj	qk	rv	LJK
B	1.0000												
DJ	0.8613	1.0000											
DJK	0.6278	0.3965	1.0000										
HJ	0.6652	0.9165	0.2116	1.0000									
HJK	0.6058	0.4903	0.9071	0.3026	1.0000								
Azeta	-0.0025	0.1238	-0.1695	0.2693	-0.1242	1.0000							
nJ	-0.0705	0.0173	-0.2097	0.0584	-0.2842	-0.0482	1.0000						
nK	0.1400	0.0547	0.2710	0.0117	0.3541	0.2849	-0.9189	1.0000					
qv	-0.1640	-0.3292	0.0340	-0.5391	0.0293	-0.5838	-0.0657	-0.0799	1.0000				
qj	-0.1938	-0.4174	0.0506	-0.6843	0.0410	-0.5079	-0.0984	0.0128	0.8825	1.0000			
qk	0.0587	0.1241	-0.0087	0.1945	-0.0346	-0.0400	0.0788	-0.3017	0.1149	-0.1667	1.0000		
rv	-0.1420	-0.2953	0.0278	-0.3705	-0.0284	-0.1857	-0.2691	0.2194	0.3108	0.3817	-0.0657	1.0000	
LJK	-0.2224	-0.3225	-0.2962	-0.2453	-0.6549	-0.0416	0.3935	-0.4390	0.0087	0.0052	0.0912	0.0874	1.0000

Results and Discussion

The oblate symmetric top PF_3 shows a strong $\Delta J=+1$, $\Delta K=0$ ground state spectrum. The $v_2=1$ rotational spectrum is also quite strong, lines are about 10 times weaker than the ground state. Due to the fluorine nuclear spin statistic for both the spectra, $K = 3n$ lines are twice those for $K \neq 3n$. The spectra in ground and $v_2=1$ states are simple, so the different k values ($k=0,1,2,3,4,\dots$) for each J transition are assigned easily. The centrifugal distortion produces a band head to high frequency at $k = 0$, with a spread to lower frequency with higher k .

If $|k|$ values are plotted against frequency for ground and $v_2=1$ states, the Fortrat diagram is produced which is shown in Figure 1. In this diagram the splitting increase as k increases and this is due to the D_{JK} parameter. In other words the term $-2D_{JK}(J+1)k^2$ has the effect of separating the $(J+1)$ components of each $(J+1) - J$ transition.

Figure 1. Fortrat diagram of PF_3 in ground and $v_2 = 1$ states. $J=20 \rightarrow 21$.

It is generally assumed that rotational Hamiltonian of a symmetric top in its ground vibrational state is diagonal in J and K . But, actually the rotation of the molecule about the b -axis produces a small distortion moment perpendicular to the symmetry axis and a new term appears in the Hamiltonian:

$$H_{\text{split}} = \epsilon[(J_+^3 + J_-^3)J_z + J_z(J_+^3 + J_-^3)] + h_3'(J_+^6 + J_-^6). \quad (6)$$

The first term has $\Delta K=\pm 3$ matrix elements and the second one $\Delta K=\pm 6$ matrix elements. ϵ and h_3' are quartic and sextic centrifugal distortion constants respectively. In reducing the Hamiltonian, the $\Delta K=\pm 3$ matrix elements are eliminated. So,

$$\tilde{H}_{\text{split}} = h_3(J_+^6 + J_-^6) \quad (7)$$

with

$$h_3 = h_3' - \frac{\epsilon^2}{B_z - B_x}. \quad (8)$$

The reduced Hamiltonian contributes in first order to the A_1/A_2 splitting of the $K = 3$ levels:

$$E_{-3,+3} = h_3 J(J+1)[J(J+1) - 2][J(J+1) - 6]. \quad (9)$$

For C_{3v} symmetric tops the splitting of the $K=3$ levels is dependent on the magnitude of the sextic constant h_3 , which is usually smaller than H_J . Cazzoli²³ and colleagues have found a strong correlation between h_3 and $B^4/(C-B)$, the result being (in MHz)

$$h_3 = 2.3 \times 10^{-21} \frac{B^4}{C-B}. \quad (10)$$

This relation can predict known values of h_3 to better than 20%. If the values of rotational constants B and C in ground state are put in Eq 10 then $h_3 = 2.836$ mHz is obtained for PF_3 , while this value has been determined 2.4982 (73) mHz⁷. Figure 2 shows

the variation of $k = 3$ splitting from $J = 26$ to $J = 82$, which increases rapidly as J increases⁷. it is obvious that submillimeter-wave spectroscopy is one of best method to observe it.

Figure 2. Variation of $K = 3$ splitting with J .

For the $v_4 = 1$ state the important parameters in determining form of the spectrum are the l-type doubling constant q_l^+ and the value of $A\zeta$. The parameter η_l which is to be regarded as a type of centrifugal distortion constant, has a negative value. As can be seen from Eq (3) this results in the positive series being displaced to lower frequency and the negative series to higher frequency.

If all the sextic constants were included in the fit, these were not only strongly correlated but also had standard deviations which were of about the same absolute magnitudes as the quantities themselves. This means that actual values are not significant in this state and constrained at the zero value.

This vibrational state is especially characterized by a very small value of $[C-B-C\zeta] = 26$ MHz, which together with a large value of the l-doubling constant $q_l^+ = 29.5$ MHz, leads to strong l-type resonances of states with $\Delta K = \Delta l = \pm 2$.

A least-squares refinement of the 215 observations was carried out using the programme¹². The results of fitting are given in Tables 6 and 7, the results are shown in Table 8. The Fortrat-like diagram in this state is shown in Figure 3.

This Table shows that most of the obtained parameters have different values and higher accuracy compare with Ref¹⁰.

Figure 3. Fortrat diagram of PF_3 for $J = 14$ in $v_4 = 1$ State.

Table 8. Comparison of rotation-vibration parameters for PF₃ in $v_4 = 1$ state.

Parameter	Smith Ref ⁵	Fit of data ⁵ by Ref ¹²	Ref ¹⁰	This work, Fit of Mixing of Refs ^{5&10} by Ref ¹²
C/MHz	4785.965*	4785.965*	4785.965*	4785.965
B/MHz	7823.0925(12)	7823.09030(20)	7823.09217 (28)	7823.09212(41)
C _z /MHz	-3010.941(11)	-3010.953(17)	-3010.93124(50)	-3010.9468(41)
D _J /kHz	7.944(3)	7.9473(43)	7.94529 (20)	7.9463(32)
D _{JK} /kHz	-11.983(15)	-12.004(22)	-12.0103(18)	-12.0371(23)
D _k /MHz	5.5*	5.5*	5.5*	5.5*
η_J /kHz	-39.8(2.4)	-43.2(36)	-40.1594 (39)	-40.371(23)
η_k /kHz	35.9(2.5)	39.2(37)	35.69 47(11)	35.798(25)
H _J /Hz	0.0*	0.0*	0.016989(32)	0.017354 (75)
H _{JK} /Hz	0.0*	0.0*	-0.0719(73)	-0.0798 (10)
H _{kJ} /Hz	0.0*	0.0*	0.09587(86)	0.0*
q _t ⁺	-29.490(2)	-29.4886(25)	29.49347(26)	-29.49200(65)
r _t /MHz	2.83(49)	3.51(72)	0.0*	2.9465(13)
q _J /kHz	-0.181(5)	-0.169(5)	0.0*	-0.16044(33)
q _k /kHz	0.37(5)	0.353(78)	0.0*	0.29527(98)
LJK/mHz	0.0*	0.0*	-0.00101*	0.03246(37)

*constrained at this value.

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