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The $A^2\Pi_i$–$X^2\Sigma^+$ System of CP: Observation of New Bands

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Infrared emission spectra of the $A^2\Pi_i$–$X^2\Sigma^+$ system of CP have been observed at high resolution using a Fourier transform infrared spectrometer. The rotational structure of seven new bands involving vibrational levels up to $v = 4$ of both electronic states has been analyzed and equilibrium molecular constants have been determined. For the $X^2\Sigma^+$ state $\omega_e = 1239.77924(8)$ cm^{-1} and $r_e = 1.5619780(2)$ Å were derived, while for the $A^2\Pi_i$ state the corresponding values are $\omega_e = 1062.47140(98)$ cm^{-1} and $r_e = 1.654420(6)$ Å.

INTRODUCTION

CP is a free radical isovalent with CN and SiN. This radical was first observed by Herzberg (*1*) who observed the $B^2\Sigma^+$–$X^2\Sigma^+$ transition which is analogous to the violet system of CN. The rotational structure of this system was analyzed by Baerwald *et al.* (*2*), who also observed the $B^2\Sigma^+$–$A^2\Pi$ transition. The rotational structure of the $B^2\Sigma^+$–$A^2\Pi$ system was also investigated by Chaudhry and Upadhya (*3*) and later by Tripathi *et al.* (*4*).

More recently we reported the first observation of the $A^2\Pi_i$–$X^2\Sigma^+$ transition of CP (*5*) (analogous to the red system of CN). In this study the rotational analysis of five vibrational bands was carried out. This work was followed by the detection of the pure rotational spectrum in the ground electronic state of CP by Saito and co-workers (*6*). These microwave measurements resolved the hyperfine structure due to the P nucleus ($I = \frac{1}{2}$). Calculations of Franck–Condon factors, r-centroids, and the potential energy curves of CP have been published by several workers (*7–10*).

CP is an excellent candidate for detection in circumstellar envelopes of stars (such as IRC + 10216) and in the interstellar medium. IRC + 10216 is a prototypical cool carbon star surrounded by a thick shell of dust and molecules. Linear carbon chain molecules such as C_n (*11, 12*), C_nH (*13*), C_nN (*14*), C_nO (*15*), C_nS (*16, 17*), and HC_nN (*18, 19*) have been found in IRC + 10216 and various other extraterrestrial sources, suggesting that the analogous phosphorous families C_nP and HC_nP might be found. CP is the first member of the C_nP family.

There is a surprisingly strong bond in the CP molecule with a large dissociation energy of 121 kcal/mole (*20–22*). This large dissociation energy also makes the detection of CP quite favorable in space. These speculations have recently been confirmed by the observation of CP in the carbon star IRC + 10216 (*23*). Other recent work on CP includes the detection of the ESR spectrum in an argon matrix and two *ab initio* calculations of molecular properties (*24, 25*).

In the present study we extend our previous work on the $A^2\Pi_i$–$X^2\Sigma^+$ transition of CP to include bands involving $v = 0$–4 of both states. We have rotationally analyzed

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TABLE I

Observed Wavenumbers of the Lines in the New *A*–*X* Bands of CP

J	R1	O-C	P1	O-C	Q1	O-C	R12	O-C	P12	O-C	Q12	O-C
					2-2 BAND							
1.5	6460.1538	21										
2.5	6461.8709	-4										
3.5	6463.4125	-3										
4.5	6464.7780	17									6449.3829	-39
5.5	6465.9622	6			6456.9283	-6					6447.6330	-9
6.5	6466.9676	-12	6447.5132	-8	6456.5455	-15	6456.1309	53			6445.7028	-5
7.5	6467.7966	-12	6445.5674	25	6455.9855	-17	6455.4059	-4			6443.5954	5
8.5	6468.4467	-19	6443.4375	-6	6455.2487	-8	6454.5076	-14			6441.3117	28
9.5			6441.1348	12	6454.3337	-1	6453.4325	-14			6438.8448	-3
10.5	6469.2148	-7	6438.6562	48	6453.2395	-7	6452.1796	-14	6421.6176	12	6436.2037	-1
11.5	6469.3315	-1	6435.9909	-8	6451.9691	3	6450.7496	-5	6417.4103	6	6433.3841	-8
12.5	6469.2722	27	6433.1549	6	6450.5193	-2	6449.1414	-1	6413.0238	-19	6430.3899	14
13.5			6430.1392	-3	6448.8917	-7	6447.3572	22	6408.4652	4	6427.2155	8
14.5	6468.6113	10	6426.9498	26	6447.0860	-15	6445.3909	1			6423.8635	1
15.5	6468.0133	-1	6423.5787	12	6445.1048	-1	6443.2497	8	6398.8079	-41	6420.3358	10
16.5	6467.2404	23	6420.0317	12	6442.9444	-1	6440.9294	2	6393.7155	-50	6416.6265	-25
17.5	6466.2851	4	6416.3060	-2	6440.6066	2	6438.4322	3	6388.4489	-33	6412.7470	11
18.5	6465.1531	2	6412.4019	-27	6438.0913	7	6435.7568	-2	6383.0083	9	6408.6862	5
19.5	6463.8414	-15	6408.3260	0	6435.3980	7	6432.9079	34	6377.3859	-2	6404.4490	6
20.5	6462.3550	3	6404.0698	-4	6432.5262	-1	6429.8765	20	6371.5904	19	6400.0347	6
21.5	6460.6901	19	6399.6379	4	6429.4815	36	6426.6674	4	6365.6140	-6	6395.4420	-9
22.5	6458.8439	3	6395.0327	49	6426.2517	-3	6423.2793	-28	6359.4650	5	6390.6739	-10
23.5	6456.8228	21	6390.2399	-14	6422.8481	-5			6353.1370	-15	6385.7265	-36
24.5	6454.6190	-7	6385.2776	-5	6419.2711	32	6415.9798	-5	6346.6388	23	6380.6113	27
25.5	6452.2395	-11	6380.1385	3	6415.5098	-1	6412.0616	-19	6339.9567	5	6375.3098	-7
26.5	6449.6827	-7	6374.8225	8	6411.5749	2	6407.9694	-2	6333.1047	-6	6369.8360	0
27.5			6369.3292	5	6407.4625	2	6403.7017	32	6326.0750	-13	6364.1861	11
28.5	6444.0354	6	6363.6644	51	6403.1715	-13	6399.2519	15	6318.8748	29	6358.3572	-6
29.5	6440.9446	11	6357.8160	24	6398.7066	4	6394.6243	-10	6311.4943	21	6352.3549	6
30.5	6437.6736	-7	6351.7917	0	6394.0639	12	6389.8250	17	6303.9362	-12	6346.1762	14
31.5	6434.2301	30	6345.5935	-2	6389.2432	10	6384.8451	6	6296.2104	28	6339.8195	3
32.5	6430.6030	10	6339.2168	-29	6384.2449	-1	6379.6886	-4	6288.3059	30	6333.2868	-10
33.5	6426.7975	-17	6332.6697	-1	6379.0703	-7	6374.3523	-45	6280.2195	-40	6326.5811	6
34.5			6325.9415	-26	6373.7205	2	6368.8487	7	6271.9651	-43	6319.6982	6
35.5	6418.6627	26	6319.0406	-21	6368.1931	0			6263.5420	11	6312.6430	39
36.5	6414.3214	-27	6311.9679	21	6362.4909	15	6357.3028	18	6254.9408	27	6305.4103	51
37.5			6304.7154	20	6356.6099	7	6351.2593	-37			6297.9953	-6
38.5			6297.2845	-12	6350.5571	44					6290.4088	-26
39.5			6289.6824	-4	6344.3197	-3					6282.6515	-4

J	R2	O-C	P2	O-C	Q2	O-C	P21	O-C	Q21	O-C
					2-2 BAND CONTINUED					
3.5					6608.4751	9				
4.5					6606.9494	-4				
5.5					6605.2586	-12				
6.5					6603.4041	-1				
7.5					6601.3846	14				
8.5					6599.1997	29				
9.5					6596.8474	26				
10.5					6594.3258	-16			6611.4670	-2
11.5			6575.6379	13	6591.6453	7			6610.3408	-0
12.5			6571.3993	15	6588.7976	13			6609.0476	-10
13.5			6566.9948	10	6585.7835	10			6607.5926	21
14.5			6562.4232	-17	6582.6037	3			6605.9621	-43
15.5	6602.5259	12	6557.6925	16	6579.2570	-19			6604.1753	-11
16.5	6600.4217	5	6552.7935	15	6575.7497	8			6602.2192	-12
17.5	6598.1509	-7	6547.7276	-5	6572.0743	7			6600.1020	36
18.5	6595.7158	-1	6542.5012	18	6568.2329	1			6597.8089	-14
19.5	6593.1152	11	6537.1047	-11	6564.2268	1			6595.3543	-19
20.5	6590.3473	11	6531.5514	40	6560.0531	-21			6592.7384	25
21.5	6587.4131	10	6525.8265	23	6555.7186	3			6589.9477	-19
22.5	6584.3085	-34	6519.9363	1	6551.2137	-24	6555.2996	-37	6586.9971	0
23.5	6581.0435	-19	6513.8843	7	6546.5489	4	6550.7826	0	6583.8815	32
24.5	6577.6113	-13	6507.6657	-5	6541.7153	-2	6546.0966	1	6580.5930	-4
25.5	6574.0175	39	6501.2838	-4	6536.7159	-13	6541.2462	11		
26.5	6570.2458	-24			6531.5514	-22	6536.2268	-16		
27.5	6566.3153	-12			6526.2247	1	6531.0459	-4		
28.5	6562.2172	-12			6520.7300	-2	6525.6979	-9		
29.5	6557.9520	-20			6515.0707	2	6520.1894	34		
30.5	6553.5223	-7			6509.2456	1	6514.5093	14		
31.5	6548.9265	9			6503.2556	5	6508.6651	7		
32.5	6544.1628	11			6497.0995	1	6502.6604	48		
33.5					6490.7795	11				
34.5					6484.2920	-1				
35.5					6477.6408	3				
36.5					6470.8221	-14				
37.5					6463.8414	1				
38.5					6456.6934	-3				
39.5					6449.3829	20				

TABLE I—*Continued*

J	R1	O-C	P1	O-C	Q1	O-C	R12	O-C	P12	O-C	Q12	O-C
					3-3 BAND							
3.5											6278.5505	-37
4.5	6292.2536	-32									6276.9872	-17
5.5	6293.4307	11			6284.4680	-17	6284.2096	28			6275.2411	-55
6.5	6294.4291	41			6284.0860	-12	6283.6668	11			6273.3263	-11
7.5	6295.2434	3	6273.1857	-37	6283.5263	-14	6282.9468	-7			6271.2303	-11
8.5	6295.8845	7	6271.0735	-15	6282.7895	-16	6282.0533	11	6257.2441	11	6268.9566	-18
9.5	6296.3479	7	6268.7827	-9	6281.8829	55	6280.9776	-23	6253.4182	22	6266.5099	12
10.5	6296.6288	-43	6266.3148	-7	6280.7887	20	6279.7308	3	6249.4167	43	6263.8802	-20
11.5	6296.7399	-18	6263.6679	-27	6279.5179	-10	6278.3021	-20	6245.2330	5	6261.0791	2
12.5	6296.6757	29	6260.8498	9	6278.0741	-1	6276.7015	7	6240.8766	3	6258.1025	34
13.5	6296.4283	18	6257.8535	28	6276.4519	-5	6274.9213	8	6236.3455	16	6254.9408	-17
14.5	6296.0033	5	6254.6750	-8	6274.6531	-6	6272.9656	24	6231.6335	-18	6251.6096	1
15.5	6295.4002	-14	6251.3240	-3	6272.6776	-4	6270.8293	2	6226.7527	19	6248.0987	-12
16.5	6294.6211	-19	6247.7966	3	6270.5266	11	6268.5165	-16	6221.6901	-2	6244.4142	3
17.5	6293.6661	-9	6244.0958	39	6268.1947	-14	6266.0353	50	6216.4557	17	6240.5551	35
18.5	6292.5336	0	6240.2099	-13	6265.6912	13	6263.3701	44	6211.0393	-27	6236.5132	3
19.5	6291.2237	10	6236.1513	-28			6260.5254	10	6205.4550	7	6232.2982	2
20.5	6289.7350	5	6231.9225	17	6260.1461	-12	6257.5012	-53			6227.9056	-14
21.5	6288.0691	2	6227.5111	-3	6257.1074	-35	6254.3087	-32			6223.3409	10
22.5	6286.2263	4	6222.9241	-18	6253.8991	12	6250.9420	13			6218.5975	7
23.5	6284.2096	40	6218.1644	0	6250.5097	14	6247.3975	45	6181.3511	14	6213.6764	-14
24.5	6282.0066	-14	6213.2284	14	6246.9411	-11	6243.6684	-5	6174.8840	-16	6208.5862	33
25.5	6279.6314	-17	6208.1121	-16	6243.1995	-2	6239.7714	30			6203.3121	-3
26.5	6277.0787	-22	6202.8217	-31	6239.2813	5	6235.6906	-9			6197.8683	22
27.5	6274.3533	18	6197.3611	9	6235.1864	9	6231.4398	14	6154.4400	-43	6192.2436	-8
28.5	6271.4441	-8	6191.7226	26	6230.9158	18	6227.0114	23			6186.4525	53
29.5	6268.3590	-22	6185.9083	39	6226.4670	7	6222.4072	36			6180.4743	-3
30.5			6179.9122	-12	6221.8418	-7	6217.6187	-35			6174.3245	-23
31.5			6173.7483	11	6217.0415	-11	6212.6675	28			6168.0062	23
32.5			6167.4045	-14			6207.5284	-30			6161.5017	-42
33.5			6160.8897	2	6206.9161	11	6202.2191	-31			6154.8341	12
34.5			6154.2000	18	6201.5895	20	6196.7394	20				
35.5					6196.0868	26						
36.5					6190.4055	2						
37.5					6184.5523	15						
38.5					6178.5211	2						
39.5					6172.3154	-2						

J	R2	O-C	P2	O-C	Q2	O-C	R21	O-C	P21	O-C	Q21	O-C
					3-3 BAND CONTINUED							
4.5					6434.5710	48						
5.5					6432.8258	0					6442.1074	-16
6.5	6441.4832	-15			6430.9832	27					6441.8076	-28
7.5	6440.8707	-37			6428.9697	-7	6453.0779	-24			6441.3493	26
8.5	6440.1010	20			6426.7975	19	6453.8339	28	6428.8116	-25	6440.7181	1
9.5	6439.1588	4			6424.4579	19	6454.4210	44	6426.6189	-19	6439.9266	24
10.5	6438.0470	-57			6421.9498	-18	6454.8333	-34	6424.2659	31	6438.9680	28
11.5	6436.7785	-33	6403.4135	25	6419.2803	-22	6455.0967	54	6421.7375	-25	6437.8386	-25
12.5	6435.3436	-21	6399.1998	13	6416.4498	11	6455.1828	24	6419.0535	10	6436.5507	-11
13.5	6433.7461	17	6394.8203	-12	6413.4525	24	6455.1043	4	6416.2028	25	6435.0958	-15
14.5	6431.9759	-20			6410.2854	-14	6454.8591	-26	6413.1862	29	6433.4766	-10
15.5	6430.0459	-1	6385.5766	19	6406.9595	7	6454.4561	23	6410.0001	-15	6431.6914	-13
16.5	6427.9491	2	6380.7055	6	6403.4655	-6	6453.8838	36	6406.6517	-35	6429.7413	-11
17.5	6425.6877	13	6375.6726	17	6399.8086	-2	6453.1418	10				
18.5	6423.2603	18	6370.4740	13	6395.9900	33	6452.2379	24	6399.4688	4	6425.3464	4
19.5	6420.6650	-3	6365.1088	-16	6392.0014	14	6451.1650	7	6395.6248	-31	6422.9014	16
20.5			6359.5839	0	6387.8478	-8	6449.9256	-16	6391.6237	9	6420.2837	-44
21.5	6414.9842	17			6383.5347	22	6448.5210	-30	6387.4532	2	6417.5111	0
22.5	6411.8894	-36	6348.0421	32					6383.1215	30	6414.5670	-16
23.5	6408.6332	-47			6374.4089	24	6445.2178	-14	6378.6166	-28	6411.4614	8
24.5	6405.2169	-3			6369.5964	-1	6443.3152	-23	6373.9536	-21	6408.1883	12
25.5	6401.6297	-13			6364.6219	0	6441.2479	-17	6369.1274	1	6404.7473	-8
26.5					6359.4842	15	6439.0136	-17	6364.1309	-34	6401.1367	-68
27.5					6354.1794	6	6436.6175	28	6358.9801	34	6397.3737	4
28.5									6353.6555	11	6393.4394	19
29.5							6431.3118	-22	6348.1687	11	6389.3370	10
30.5							6428.4134	-5			6385.0676	-13
31.5							6425.3464	-8				

seven new bands, 2–2, 3–3, 3–1, 1–3, 2–0, 4–3, and 2–4. The molecular constants obtained in this study, combined with our previous data, provide improved equilibrium constants for both electronic states. These constants were used in the calculation of potential energy curves for the $A^2\Pi$ and $X^2\Sigma^+$ states and the Franck–Condon factors for the A–X system.

TABLE I—*Continued*

J	R1	O-C	P1	O-C	Q1	O-C	R12	O-C	P12	O-C	Q12	O-C
					1-3 BAND							
4.5	4227.9472	68			4220.2409	54					4212.5479	-15
5.5	4229.2645	58			4220.1547	14					4210.9306	4
6.5	4230.4274	54									4209.1523	-42
7.5	4231.4363	60			4219.5291	44	4219.1344	-4			4207.2284	1
8.5	4232.2886	49			4218.9776	-8	4218.4581	60				
9.5	4232.9863	41	4204.9684	-25	4218.2770	-3	4217.6178	29			4202.9093	7
10.5	4233.5268	12	4202.7148	-6	4217.4220	3	4216.6245	16			4200.5176	4
11.5	4233.9167	27	4200.3074	18	4216.4108	-6	4215.4718	-46			4197.9711	-3
12.5	4234.1485	11	4197.7412	-2	4215.2474	10	4214.1724	-29	4177.7687	0	4195.2728	15
13.5			4195.0271	41	4213.9294	25	4212.7236	39	4173.5143	-19		
14.5	4234.1485	-6			4212.4522	-7			4169.1120	21	4189.4083	-4
15.5	4233.9167	-7	4189.1231	-4	4210.8232	-11	4209.3455	7	4164.5477	-23	4186.2452	-10
16.5	4233.5268	-39	4185.9433	7	4209.0393	-19	4207.4249	-8	4159.8405	39	4182.9304	7
17.5	4232.9863	-27	4182.6086	9	4207.1011	-26	4205.3506	-16	4154.9615	-82	4179.4607	15
18.5	4232.2886	-37	4179.1196	8	4205.0123	4	4203.1237	-7	4149.9511	15	4175.8345	-4
19.5	4231.4383	-24	4175.4765	4	4202.7664	8	4200.7376	-47	4144.7769	6	4172.0578	10
20.5	4230.4314	-26	4171.6797	1	4200.3655	4	4198.2049	-10	4139.4487	-11	4168.1245	-4
21.5	4229.2702	-23	4167.7318	25	4197.8110	7	4195.5253	100			4164.0393	0
22.5	4227.9530	-30	4163.6260	6	4195.1023	10			4128.3360	-22	4159.7990	-13
23.5	4226.4822	-24	4159.3704	25	4192.2408	25					4155.4076	-2
24.5	4224.8579	-5	4154.9544	-26	4189.2212	1	4186.5173	-18	4116.6160	4	4150.8621	2
25.5			4150.3936	9	4186.0501	2	4183.2100	-24	4110.5228	-27	4146.1627	0
26.5			4145.6747	-5	4182.7245	-4					4141.3108	4
27.5	4219.0503	-6	4140.8043	-1	4179.2482	23	4176.1330	-45	4097.8902	19	4136.3055	6
28.5	4216.8038	-18	4135.7809	3	4175.6122	-9	4172.3675	-20	4091.3414	-2	4131.1471	6
29.5	4214.4063	7	4130.6035	-2	4171.8268	1	4168.4474	-4			4125.8342	-10
30.5			4125.2749	8	4167.8812	-54			4077.7902	-21	4120.3722	10
31.5			4119.7931	15	4163.7933	4			4070.7924	23	4114.7581	36
32.5			4114.1551	-14	4159.5466	8			4063.6368	4	4108.9834	-18
33.5			4108.3695	7	4155.1427	-26					4103.0637	2
34.5			4102.4279	-9	4150.5916	1					4096.9844	-52
35.5					4145.8855	10					4090.7608	-26
36.5					4141.0246	3					4084.3883	32
37.5					4136.0098	-14					4077.8537	-13
38.5					4130.8450	0					4071.1717	-13
39.5					4125.5265	3						

J	R2	O-C	P2	O-C	Q2	O-C	R21	O-C	P21	O-C	Q21	O-C
					1-3 BAND CONTINUED							
2.5					4372.8926	-12						
3.5					4371.6195	-33						
4.5					4370.2056	-41						
5.5												
6.5			4357.8285	-26	4366.9534	-36	4388.3102	-10				
7.5			4354.5873	-9	4365.1163	-13			4366.8164	-26	4377.4863	-17
8.5			4351.2031	-2	4363.1313	-47	4390.3913	37	4364.9650	38	4377.0513	-5
9.5	4375.9447	-8	4347.6863	96	4361.0122	-2	4391.2101	-16	4362.9638	26	4376.4702	-31
10.5	4375.1012	8	4344.0114	31	4358.7472	5	4391.8946	14			4375.7533	10
11.5	4374.1084	-45	4340.2023	42	4356.3366	-24	4392.4320	1	4358.5344	-7	4374.8848	-40
12.5	4372.9829	0	4336.2467	5	4353.7872	-21	4392.8278	0	4356.1088	-2	4373.8821	-8
13.5	4371.7081	-23	4332.1525	-1	4351.0933	-42	4393.0809	1	4353.5417	8	4372.7342	-3
14.5	4370.2938	-15	4327.9208	34					4350.8309	2	4371.4458	22
15.5	4368.7387	11	4323.5438	31					4347.9803	18	4370.0066	-35
16.5	4367.0405	31	4319.0216	-8			4392.9822	3	4344.9858	15		
17.5			4314.3619	-6	4338.9140	36	4392.6621	-7	4341.8488	6	4366.7132	-22
18.5	4363.2097	7	4309.5602	-11	4335.5061	-26	4392.2008	2	4338.5699	-1	4364.8539	-2
19.5	4361.0828	20	4304.6178	-7	4331.9627	-23						
20.5	4358.8079	-20	4299.5341	-3	4328.2741	-53	4390.8472	8				
21.5	4356.3975	13	4294.3098	9	4324.4545	27	4389.9524	-20			4358.4144	1
22.5	4353.8408	10	4288.9361	-60			4388.9195	5			4355.9815	-7
23.5	4351.1414	8	4283.4345	4			4387.7434	32			4353.4054	-20
24.5							4386.4235	56			4350.6893	-6
25.5											4347.8273	-22
26.5							4383.3416					
27.5							4381.5898	4				
28.5							4379.6931	5				

EXPERIMENTAL DETAILS

The emission spectra of CP were observed in two separate experiments. In the first spectrum (used in the previous analysis) CP bands were observed in a microwave discharge of a mixture of 0.04 Torr of white phosphorous vapor and 0.4 Torr of H_2 in a quartz cell. This cell was previously used in experiments with methane so the

TABLE I—*Continued*

J	R1	O-C	P1	O-C	Q1	O-C	R12	O-C	P12	O-C	Q12	O-C
						2-0 BAND						
0.5	8896.8274	-13										
1.5	8898.7045	22										
2.5	8900.3754	15			8895.5118	23	8895.6530	-15			8890.7934	33
3.5	8901.8440	6			8895.5956	61	8895.5559	49			8889.2945	-25
4.5	8903.1103	-6	8889.2165	31	8895.4682	7	8895.2430	-27			8887.6018	-3
5.5	8904.1728	-35	8887.5028	28	8895.1439	3			8878.0565	-55	8885.7050	-4
6.5	8905.0403	8	8885.5884	37	8894.6218	40	8894.0319	26	8874.5742	-1	8883.6043	-27
7.5	8905.7016	10	8883.4659	-18	8893.8883	-17	8893.1156	-26	8870.8846	-5	8881.3091	22
8.5	8906.1586	-9	8881.1470	-20	8892.9598	-6	8892.0055	3	8866.9944	-1	8878.8090	39
9.5	8906.4153	-9	8878.6308	21	8891.8289	1	8890.6877	-27	8862.9069	44	8876.1003	-13
10.5	8906.4690	-17	8875.9049	-17	8890.4961	7	8889.1714	-23	8858.6084	-8	8873.1972	7
11.5	8906.3234	4	8872.9841	11	8888.9603	1	8887.4539	-13	8854.1132	-15	8870.0924	24
12.5	8905.9714	-16	8869.8567	-12	8887.2225	-6	8885.5328	-20	8849.4191	0	8866.7818	-1
13.5	8905.4219	12	8866.5298	-14	8885.2857	16	8883.4122	-4	8844.5215	-9	8863.2720	-3
14.5	8904.6677	15	8863.0032	1	8883.1476	42	8881.0911	24	8839.4246	-2	8859.5605	-9
15.5	8903.7099	5	8859.2735	-1	8880.8012	3	8878.5654	23	8834.1255	-8	8855.6443	-48
16.5	8902.5500	-4	8855.3430	3	8878.2582	15	8875.8347	-10	8828.6239	-31	8851.5364	9
17.5	8901.1875	-16	8851.2083	-23	8875.5099	-9	8872.9068	1	8822.9282	11	8847.2201	-6
18.5	8899.6231	-24	8846.8775	3	8872.5617	-15	8869.7760	-1	8817.0264	-1	8842.7045	-3
19.5	8897.8599	2	8842.3480	53	8869.4102	-38	8866.4437	-2	8810.9196	-59	8837.9868	-10
20.5	8895.8877	-39	8837.6077	6	8866.0629	-3	8862.9069	-32	8804.6213	-28	8833.0705	8
21.5	8893.7213	1	8832.6685	-20	8862.5138	29	8859.1759	10	8798.1192	-32	8827.9548	40
22.5	8891.3504	17	8827.5327	-3	8858.7571	0	8855.2387	5	8791.4185	-21	8822.6295	-14
23.5	8888.7748	8	8822.1944	-2	8854.8017	-2	8851.1010	9	8784.5203	16	8817.1075	-28
24.5	8885.9963	-7	8816.6548	-6	8850.6455	3	8846.7626	19	8777.4157	-11	8811.3896	7
25.5	8883.0177	-2	8810.9196	41	8846.2868	-4	8842.2172	-28	8770.1108	-44	8805.4688	18
26.5	8879.8401	34	8804.9747	-3	8841.7326	46	8837.4780	-1	8762.6134	-4	8799.3440	-5
27.5	8876.4548	15	8798.8352	13	8836.9675	0	8832.5356	6	8754.9102	-26	8793.0210	-5
28.5	8872.8667	-12	8792.4883	-41	8832.0050	-8	8827.3871	-37	8747.0135	11	8786.4995	13
29.5	8869.0780	-24	8785.9477	-28	8826.8488	57	8822.0449	-7	8738.9081	-45	8779.7740	-7
30.5	8865.0931	22	8779.2091	7	8821.4799	6	8816.4970	-24	8730.6144	8	8772.8501	-8
31.5	8860.8997	3	8772.2671	11	8815.9144	-2	8810.7499	-25	8722.1155	0	8765.7273	2
32.5	8856.5058	-2	8765.1248	11	8810.1491	2	8804.8033	-12	8713.4165	-19	8758.4032	-1
33.5	8851.9110	3	8757.7813	0	8804.1823	-2	8798.6581	23			8750.8815	19
34.5	8847.1121	-14	8750.2373	-17	8798.0157	4	8792.3044	-21	8695.4316	36	8743.1550	-12
35.5	8842.1150	6	8742.4969	-1	8791.6487	13	8785.7524	-42	8686.1359	10	8735.2301	-30
36.5	8836.9162	26	8734.5535	-18	8785.0797	8	8779.0104	42	8676.6445	12	8727.1100	-4
37.5	8831.5068	-43	8726.4198	57					8666.9499	-36	8718.7869	-14
38.5	8825.9101	32	8718.0724	-10	8771.3455	50			8657.0623	-33	8710.2654	-14
39.5	8820.1006	-4	8709.5343	9	8764.1695	-12					8701.5457	-4

J	R2	O-C	P2	O-C	Q2	O-C	R21	O-C	P21	O-C	Q21	O-C
					2-0 BAND CONTINUED							
2.5					9048.2612	-30						
3.5					9046.8118	24						
4.5					9045.1640	-11	9060.7409	42				
5.5			9035.6689	-37	9043.3295	-18	9061.8759	-13				
6.5			9032.2566	-6	9041.3060	-20						
7.5	9051.0907	-5	9028.6549	24	9039.0985	33	9063.5940	55	9041.1735	48		
8.5	9050.0968	-24	9024.8558	-28	9036.6926	-4	9064.1621	29			9050.9303	-30
9.5	9048.9202	29	9020.8748	-6	9034.1014	1	9064.5478	80	9036.5138	-28	9049.9272	44
10.5	9047.5437	-20	9016.6977	-54	9031.3159	-42			9033.9112	49	9048.7253	29
11.5	9045.9822	-20	9012.3411	-5	9028.3491	-5			9031.1068	2	9047.3296	-26
12.5	9044.2403	75	9007.7870	-41	9025.1872	-24			9028.1206	31	9045.7528	7
13.5			9003.0525	11	9021.8425	23			9024.9416	27	9043.9871	49
14.5			8998.1231	3	9018.2989	-24			9021.5796	87	9042.0239	16
15.5	9037.8392	2	8993.0052	8	9014.5704	-27					9039.8687	-37
16.5	9035.3298	21	8987.6946	-39	9010.6551	-3			9014.2717	50	9037.5304	-22
17.5	9032.6296	32	8982.1990	-39	9006.5459	-25			9010.3276	-29	9035.0048	20
18.5	9029.7338	-12	8976.5163	-22	9002.2482	-37			9006.2033	-16	9032.2781	-48
19.5	9026.6557	22	8970.6439	-13	8997.7715	54			9001.8914	15	9029.3732	3
20.5	9023.3841	23	8964.5862	32	8993.0917	9			8997.3921	66	9026.2764	35
21.5					8988.2300	38			8992.6880	-36	9022.9831	3
22.5	9016.2701	22	8951.8925	2	8983.1728	6					9019.4979	-43
23.5			8945.2589	-49	8977.9268	-19					9015.8310	-6
24.5			8938.4477	11	8972.4978	19					9011.9740	33
25.5			8931.4444	37	8966.8758	21					9007.9202	7
26.5			8924.2483	22	8961.0626	5					9003.6789	9
27.5			8916.8580	-49	8955.0588	-23						
28.5			8909.2907	-3	8948.8687	-19					8994.6254	15
29.5			8901.5281	-25	8942.4936	28					8989.8096	-16
30.5			8893.5784	-32	8935.9201	-15						
31.5			8885.4404	-37	8929.1661	31						
32.5			8877.1221	40	8922.2145	-5						
33.5			8868.6044	7	8915.0771	-4						
34.5			8859.8999	-8	8907.7481	-26						
35.5			8851.0063	-31	8900.2342	-2						
36.5			8841.9327	31	8892.5276	-11						

TABLE I—*Continued*

J	R2	O-C	P2	O-C	Q2	O-C	R21	O-C	P21	O-C	Q21	O-C
					3-1 BAND							
5.5			8835.9345	2							8852.9508	-38
6.5			8832.5351	-55			8862.8590	-64			8852.5104	-13
7.5			8828.9566	-15	8839.3058	-60	8863.6125	-8	8841.3678	-77		
8.5	8850.2209	-31	8825.1913	42	8836.9162	-44	8864.1753	36	8839.1501	-45	8851.0601	15
9.5	8849.0377	-53	8821.2308	33	8834.3415	9	8864.5396	-11	8836.7489	40	8850.0482	7
10.5	8847.6716	-12			8831.5732	14	8864.7184	-19			8848.8515	27
11.5	8846.1133	-1	8812.7415	-11	8828.6229	88	8864.7071	-32	8831.3646	55	8847.4556	-45
12.5	8844.3661	14	8808.2174	0	8825.4667	-10	8864.5144	36	8828.3842	13	8845.8832	10
13.5	8842.4339	71	8803.5046	7	8822.1339	14	8864.1220	4	8825.2213	33	8844.1176	26
14.5	8840.2992	-3	8798.6045	26	8818.6101	17			8821.8629	-13	8842.1599	13
15.5	8837.9868	40	8793.5078	-38	8814.8973	17	8862.7700	-40	8818.3270	53	8840.0141	13
16.5	8835.4768	0	8788.2340	11	8810.9900	-41	8861.8194	40			8837.6755	-21
17.5	8832.7777	-36	8782.7641	-18	8806.9042	5	8860.6670	0	8810.6735	31	8835.1574	43
18.5	8829.8976	12	8777.1121	15	8802.6209	-37	8859.3276	-11	8806.5628	13	8832.4397	6
19.5					8798.1565	-2	8857.7967	-36	8802.2607	-32	8829.5375	18
20.5			8765.2383	28	8793.5050	49	8856.0820	1	8797.7786	11	8826.4418	-11
21.5	8820.1011	-36	8759.0174	18	8788.6514	-33	8854.1755	21	8793.1007	-17	8823.1596	-9
22.5	8816.4611	-5	8752.6088	12	8783.6196	-9	8852.0759	13	8788.2341	-44	8819.6903	18
23.5	8812.6255	-34	8746.0096	-19	8778.4012	36	8849.7915	59	8783.1891	33	8816.0241	-28
24.5	8808.6020	-46	8739.2267	-5	8772.9900	41			8777.9413	-31	8812.1707	-51
25.5	8804.3993	47	8732.2567	17	8767.3823	-31	8844.6336	-29	8772.5151	9	8808.1296	-53
26.5	8799.9987	59	8725.0937	-10			8841.7771	8	8766.9005	52	8803.9028	-16
27.5	8795.4037	24			8755.6234	52	8838.7255	-1	8761.0822	-54	8799.4848	7
28.5	8790.6159	-40	8710.2101	0	8749.4530	15			8755.0909	-2	8794.8688	-53
29.5	8785.6507	20			8743.0931	-29			8748.9102	43	8790.0709	-34
30.5	8780.4976	99	8694.5726	-11	8736.5539	22			8742.5387	68	8785.0797	-49
31.5			8686.4757	20	8729.8171	-16					8779.9103	53
32.5			8678.1859	1	8722.8955	-14			8729.2181	5	8774.5372	16
33.5			8669.7044	-56	8715.7833	-30					8768.9818	56
34.5			8661.0474	9	8708.4870	0					8763.2295	28
35.5			8652.1990	38	8701.0004	15						
36.5					8693.3195	-24						
37.5												
38.5					8677.3999	-19						

J	R1	O-C	P1	O-C	Q1	O-C	R12	O-C	P12	O-C	Q12	O-C
					4-3 BAND							
3.5											7292.7065	39
4.5											7291.0888	20
5.5	7307.3931	2			7298.5013	-47						
6.5	7308.3065	22			7298.0499	-8	7297.5453	3			7287.2962	54
7.5					7297.4113	43	7296.7302	-13			7285.1134	28
8.5	7309.5610	-3			7296.5776	25					7282.7428	4
9.5	7309.9046	-23			7295.5512	-37	7294.5387	-10			7280.1865	4
10.5			7279.9922	-7	7294.3445	-20	7293.1609	-5	7263.0887	-12	7277.4416	-3
11.5			7277.2312	9	7292.9503	5	7291.5948	0	7258.7981	58	7274.5107	10
12.5			7274.2826	29	7291.3645	-3	7289.8392	-9			7271.3887	-9
13.5	7309.4029	0	7271.1379	-33	7289.5905	-12	7287.9000	29	7249.6293	-52	7268.0775	-41
14.5			7267.8121	-27	7287.6267	-36	7285.7669	8	7244.7742	-4	7264.5852	-7
15.5	7308.0186	-5	7264.3008	1	7285.4805	-4	7283.4496	27	7239.7276	1	7260.9026	1
16.5	7307.0449	8	7260.5984	-5	7283.1444	11	7280.9446	50			7257.0312	-1
17.5	7305.8816	11	7256.7065	-29	7280.6210	34	7278.2499	56	7229.0720	2	7252.9733	7
18.5	7304.5275	-7	7252.6264	-58	7277.9027	-12	7275.3594	-15			7248.7228	-36
19.5	7302.9873	0	7248.3666	-10			7272.2864	-32			7244.2912	-15
20.5			7243.9163	8	7271.9157	32	7269.0239	-65			7239.6715	0
21.5	7299.3388	-8	7239.2746	-14	7268.6367	18					7234.8616	-15
22.5	7297.2325	-3	7234.4496	5	7265.1689	-5	7261.9529	44			7229.8667	-7
23.5	7294.9368	-6	7229.4373	23	7261.5151	-10	7258.1241	-17			7224.6855	9
24.5	7292.4525	-9	7224.2334	-4	7257.6786	35	7254.1200	45			7219.3162	15
25.5	7289.7818	9	7218.8486	31	7253.6449	-14	7249.9127	-48			7213.7594	16
26.5	7286.9226	28	7213.2656	-46	7249.4306	7	7245.5314	-5			7208.0162	22
27.5	7283.8663	-40	7207.5045	-35	7245.0291	32	7240.9552	-36			7202.0845	12
28.5	7280.6204	-99	7201.5633	44	7240.4375	31	7236.2000	18			7195.9642	-18
29.5	7277.2102	44	7195.4133	-99	7235.6556	2	7231.2505	2			7189.6591	-29
30.5			7189.0990	-18	7230.6887	-4					7183.1692	-23
31.5			7182.5949	30	7225.5370	16					7176.4954	9
32.5			7175.8993	28							7169.6302	-10
33.5					7214.6680	16						
34.5					7208.9521	9						
35.5					7203.0408	-82						
36.5					7196.9612	13						
37.5					7190.6803	-36						
38.5					7184.2216	5						

TABLE I—*Continued*

J	Q1	O-C	R12	O-C	Q12	O-C
			2-4 BAND			
4.5					4065.9251	-11
5.5					4064.3212	33
6.5					4062.5549	-11
7.5	4072.8394	-14			4060.6436	32
8.5	4072.2982	22			4058.5710	-3
9.5	4071.5962	-13			4056.3465	-22
10.5	4070.7400	-51			4053.9708	-17
11.5	4069.7367	-23			4051.4432	2
12.5	4068.5772	-20				
13.5	4067.2673	17	4066.0639	-2	4045.9266	28
14.5			4064.4613	-3		
15.5	4064.1795	19				
16.5	4062.4042	10	4060.7926	-33		
17.5	4060.4784	31	4058.7380	53		
18.5	4058.3949	11	4056.5166	5		
19.5	4056.1589	0				
20.5	4053.7689	-16				
21.5	4051.2258	-30				
22.5						
23.5	4045.6842	-14				
24.5	4042.6866	24				

carbon atoms required for the formation of CP were deposited on the walls of the discharge cell. This experiment was originally designed to produce the vibration–rotation bands of PH (*26*). In the second spectrum (used in this analysis) a mixture of 0.04 Torr of white phosphorous vapor, 2.75 Torr of He, and 0.03 Torr of CH_4 was used in the same discharge tube. The spectra obtained in these experiments were extremely rich with strong spectra of CP (*5*), CH (*27, 28*), PH (*26*), P_2, CN, C_2 (*29, 30*), and C_3 (*31*).

In fact, the new bands of CP were noticed because of the presence of the 2–2 band near the C_3 triplet system (*31*). The emission from the discharge was focused on the entrance aperture of the McMath Fourier transform spectrometer of the National Solar Observatory at Kitt Peak. InSb detectors and silicon filters limited the band pass to the 1800–9000 cm^{-1} spectral region. An unapodized resolution of 0.02 cm^{-1} was used in these experiments. A total of 10 and 9 scans were co-added, respectively, in 70 and 65 min of integration. The spectra were calibrated using the measurements of the vibration–rotation lines of CO (*32*) impurity present in the spectra. The absolute accuracy of the calibration is estimated to be better than ± 0.001 cm^{-1}.

RESULTS AND DISCUSSION

The spectral line positions were extracted from the spectra using the data reduction program PC-DECOMP developed at Kitt Peak by J. Brault. The peak positions were found by fitting a Voigt lineshape function to each feature using a nonlinear least-squares procedure. Since the spectra are very congested, we proceeded by initially predicting the line positions and then picking out and assigning just a few lines. The preliminary fit of these lines provided an accurate prediction of the remaining lines. The search for new bands involving the higher vibrational levels in both the states was guided by a preliminary Franck–Condon calculation.

The seven new bands identified and analyzed in the present study are 2–2, 3–3, 2–0, 3–1, 1–3, 4–3, 2–4. The structure of 4–3 and 2–4 bands is very weak so the $^2\Pi_{1/2}$–

TABLE II

Hyperfine-Free Pure Rotational Transitions of CP (in cm^{-1})

N'-N"	J'- J"	ν(Corrected)
2-1	2.5-1.5	3.19276644(121)
2-1	1.5-0.5	3.17420027(229)
3-2	3.5-2.5	4.784426359(88)
3-2	2.5-1.5	4.76585910(-5)
5-4	5.5-4.5	7.96743092(10)
5-4	4.5-3.5	7.94886265(43)
6-5	6.5-5.5	9.55870811(-47)
6-5	5.5-4.5	9.54014160(27)
7-6	7.5-6.5	11.14979550(-54)
7-6	6.5-5.5	11.13122800(-79)

$^2\Sigma^+$ subbands could not be identified with certainty. The assignment of the new bands was straightforward using combination differences and estimates of the rotational constants for the higher vibrational levels based on the data provided in our previous study (*5*). The observed line positions and their rotational assignments are provided in Table I.

Initially, band-by-band fits of the line positions listed in Table I were made utilizing the effective Hamiltonian of Brown *et al.* (*33*). Matrix elements for this Hamiltonian are listed by Amiot *et al.* (*34*) for $^2\Pi$ states and Douay *et al.* (*35*) for $^2\Sigma$ states. In the final fit the observed transition wavenumbers of all the bands, together with the hyperfine-free pure rotational transition wavenumbers (Table II) were fitted to determine the molecular constants provided in Tables III and IV. The pure rotational transition frequencies provided by Saito *et al.* (*6*) were corrected for the effects of hyperfine structure so that they could be introduced directly into our fits. For the 4–3 band the constants A_4, A_{D4}, and q_4 were fixed to extrapolated values, since the $^2\Pi_{1/2}$–$^2\Sigma^+$ subband involving the $v' = 4$ level was not measured.

The constants of Tables III and IV were utilized to determine the equilibrium constants in both electronic states using the expressions

$$G(v) = \omega_e(v + \tfrac{1}{2}) - \omega_e x_e(v + \tfrac{1}{2})^2 + \omega_e y_e(v + \tfrac{1}{2})^3$$

$$B_v = B_e - \alpha_e(v + \tfrac{1}{2}) + \gamma_e(v + \tfrac{1}{2})^2.$$

TABLE III

Molecular Constants for the $X\,^2\Sigma^+$ State of CP (in cm^{-1}; One Standard Deviation in Parentheses)

Constant	v = 0	v = 1	v = 2	v = 3	v = 4
T_v	0.0	1226.12726(21)	2438.57459(20)	3637.33379(26)	4822.3965(10)
B_v	0.79588102(3)	0.78989532(59)	0.78389287(65)	0.77787438(98)	0.7718384(84)
10^6x D_v	1.32794(29)	1.33169(40)	1.33620(47)	1.34310(76)	1.347(15)
10^2x γ_v	1.8567250(27)	1.849675(56)	1.844718(60)	1.839951(75)	1.83215(57)

TABLE IV

Molecular Constants for the $A^2\Pi_i$ State of CP (in cm^{-1}; one standard deviation in parentheses)

Constant	v = 0	v = 1	v = 2	v = 3	v = 4
T_v	6884.00555(15)	7934.41442(17)	8972.76553(21)	9999.06509(26)	11013.31730(50)
A_v	-156.24385(16)	-156.12670(23)	-156.04318(28)	-156.01186(27)	-156.0513[a]
10^5x A_{Dv}	4.868(18)	4.269(32)	3.022(46)	0.534(48)	0.534[a]
B_v	0.70927628(42)	0.70364924(50)	0.69801488(70)	0.69237961(90)	0.6867240(20)
10^6x D_v	1.28046(34)	1.28306(38)	1.28519(56)	1.28964(66)	1.2937(16)
10^3x p_v	9.414(14)	9.442(18)	9.655(29)	10.175(14)	14.3(13)
10^5x q_v	-4.797(67)	-4.873(93)	-4.886(9)	-4.94(11)	-4.94[a]
10^7x p_{Dv}	-1.28(11)	-1.04(16)	-1.04(36)	-1.04*	-1.04[a]

[a] Fixed values; see text.

TABLE V

Equilibrium Vibrational and Rotational Constants for the $X^2\Sigma^+$ and $A^2\Pi_i$ States of CP (in cm^{-1})

Constant	$X^2\Sigma^+$	$A^2\Pi_i$
ω_e	1239.79924(8)	1062.47140(98)
$\omega_e x_e$	6.833769(46)	6.03277(50)
10^2x $\omega_e y_e$	-0.13769(72)	0.0897(72)
B_e	0.798867748(82)	0.7120871(26)
10^2x α_e	0.596933(19)	0.56203(34)
10^5x γ_e	-0.8229(56)	-0.323(83)
r_e	1.5619780(2)	1.654420(7)Å

TABLE VI

Turning Points of the RKR Potential Energy Curve of the $A^2\Pi_i$ State of CP

v	E(v) (cm^{-1})[a]	r_{min} (Å)	r_{max} (Å)
0.0	7502.2059	1.5970	1.7184
0.5	8028.9181	1.5750	1.7471
1.0	8552.6149	1.5587	1.7700
1.5	9073.2971	1.5454	1.7900
2.0	9590.9658	1.5340	1.8081
2.5	10105.6216	1.5239	1.8250
3.0	10617.2657	1.5149	1.8408
3.5	11125.8987	1.5066	1.8559
4.0	11631.5216	1.4990	1.8704
5.0	12633.7407	1.4853	1.8980

[a] Calculated relative to the minimum of the $X^2\Sigma^+$ potential curve of the value of cm^{-1}.

TABLE VII

Turning Points of the RKR Potential Energy Curve of the $X^2\Sigma^+$ State of CP

v	E(v) (cm^{-1})	r_{min} (Å)	r_{max} (Å)
0.0	618.2003	1.5087	1.6211
0.5	1232.9734	1.4882	1.6476
1.0	1844.3276	1.4731	1.6687
1.5	2452.2618	1.4607	1.6871
2.0	3056.7749	1.4501	1.7038
2.5	3657.8661	1.4407	1.7193
3.0	4255.5341	1.4322	1.7339
3.5	4849.7781	1.4245	1.7477
4.0	5440.5969	1.4174	1.7610
5.0	6611.9549	1.4046	1.7863

The final equilibrium constants thus obtained are provided in Table V. These constants were used as input to an RKR program to calculate the classical turning points of the $A^2\Pi_i$ and $X^2\Sigma^+$ potential energy curves (Tables VI and VII). Figure 1 is a plot of the potential energy curves of the $A^2\Pi_i$ and $X^2\Sigma^+$ states of CP.

The RKR potential curves were used to calculate the Franck–Condon factors for the $A^2\Pi_i$–$X^2\Sigma^+$ system (Table VIII). The observed relative intensity of various bands follows the predictions based on the Franck–Condon factors. The values of B_e' and B_e'' result in r_e values of 1.5619780(2) and 1.654421(7) Å for $X^2\Sigma^+$ and $A^2\Pi_i$ states, respectively.

The inclusion of the hyperfine-free microwave transition frequencies in our fits results in a very precise determination of the rotational constants in the ground vibrational state. The pure rotational transitions also help break correlations between constants of the $A^2\Pi$ and $X^2\Sigma^+$ states. The constants provided in Tables II and III are in good agreement with the constants obtained in our previous study, except for $v' = 3$, because only the $^2\Pi_{3/2}$–$^2\Sigma^+$ subband of the 3–1 band was included in the previous analysis.

TABLE VIII

Franck–Condon Factors for the $A^2\Pi_i$–$X^2\Sigma^+$ System of CP

v" / v'	0	1	2	3	4
0	0.2835E0	0.3907E0	0.2310E0	0.7680E-1	0.1581E-1
1	0.3240E0	0.1884E-1	0.1352E0	0.2845E0	0.1743E0
2	0.2134E0	0.6721E-1	0.1478E0	0.4140E-2	0.1988E0
3	0.1070E0	0.1700E0	0.2411E-2	0.1489E0	0.2849E-1
4	0.4548E-1	0.1601E0	0.5411E-1	0.6174E-1	0.6946E-1

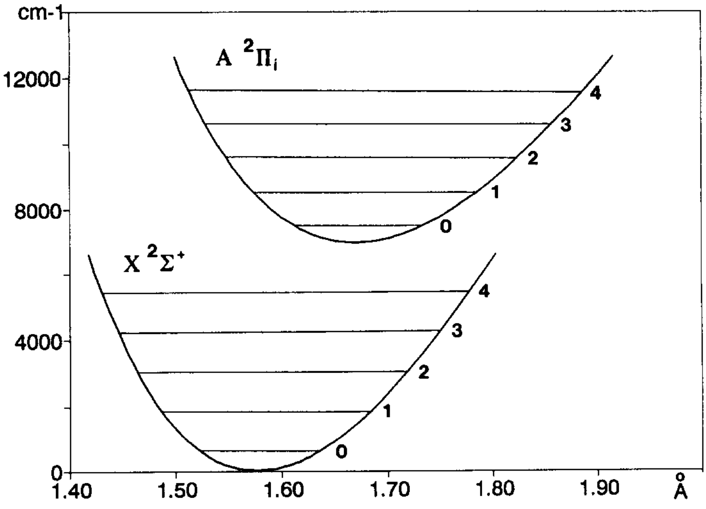

FIG. 1. Potential energy curves for the $A^2\Pi_i$ and $X^2\Sigma^+$ electronic states of CP.

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