

The B-A system of CP molecule

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Abstract. The B-A system of CP molecule has been reinvestigated. The rotational structures in the (0, 0) and (1, 1) bands have been photographed in the second order of a 10.6 m grating with 25μ slit width. The molecular constants have been determined using a weighted least squares fit computer program. It is found that the spin-splitting constant in the B-state is negative and not positive as reported by previous workers. An accurate value of α in the A-state could be determined. The present analysis also suggests that the spin-splitting constant in the ground state of CP should be positive, hence the assignment of the R_1 and R_2 or P_1 and P_2 branches in the B-X system of CP by Barwald *et al* should be interchanged.

Keywords. Spin-splitting; rotation vibration interaction constants; perturbations.

1. Introduction

The spectral study of compounds containing carbon atom is important in astrophysics, combustion flame sources and in many other branches in chemical spectroscopy. Though the spectrum of CN molecule has been studied extensively, information available about the isoelectronic molecule carbon monophosphide is very sketchy. Two band systems B-X (2900–4000 Å) and B-A (4390–4660 Å) are known in this molecule. The rotational structure in B-X system of this was analysed by Barwald *et al* (1934). On the basis of this analysis they reported the spin-splitting constant (γ) in the B-state to be positive and in the X-state to be negative. They also determined an approximate rotational constant for the A-state in the B-A system. The structure in the (0, 0) band of this system was later rotationally analysed by Chaudhary and Upadhyya (1969) who also reported γ in the B-state to be positive. A comparison of the γ in the isoelectronic molecules (such as SiN, N_2^+ , Co^+ , A10, etc.) suggest that γ in the B-state of carbon monophosphide molecule should be negative and, positive in the X-state. It is remarkable that rotational perturbations have been reported in the zeroth level of the B-state by Barward *et al* (1934) whereas Chaudhary and Upadhyya (1969) were not able to mark it. These factors prompted us to re-investigate the spectrum of CP molecule. Since it is difficult to judge the sign of spin-splitting constant in the ${}^2\Sigma$ state in a ${}^2\Sigma - {}^2\Sigma$ transition unless one observes the structure at very low temperature. We selected B-A system for our study. The second reason for the selection of B-A system is that the equilibrium constant B_e , Λ -doubling p etc are not well known for the A ${}^2\Pi$ state. The present investigation confirms that the spin-splitting constant in the B-state is certainly negative and in the

X-state it is positive. Precise molecular constants for the B and A states have been determined.

We have rephotographed the spectrum in the second order of a 10.6 m concave grating spectrograph with 0.33 Å/mm as reciprocal dispersion and resolution $> 3 \times 10^5$. The experimental arrangement for recording the spectrum was exactly the same as described by Chaudhary and Upadhyaya (1969) except that we had reduced the slit width to 25 μ . Our attempts to record the (1, 0) and (0, 1) bands even under increased slit width condition (40 μ) were futile and we had to limit ourselves with the (0, 0) and (1, 1) bands.

2. Rotational analysis

The B-state of CP molecule is a ${}^2\Sigma^+$ whereas the A-state is ${}^2\Pi_t$. The two subsystems viz. ${}^2\Sigma^+ - {}^2\Pi_{1/2}$ and ${}^2\Sigma - {}^2\Pi_{3/2}$ are separated by 157.87 cm^{-1} which is equal to the spin orbit coupling constant in the $A^2\Pi$ state. Due to the inverted nature of the ${}^2\Pi$ state, the ${}^2\Sigma - {}^2\Pi_{3/2}$ subsystem lies in the violet to the ${}^2\Sigma - {}^2\Pi_{1/2}$ subsystem.

The rotational structure in the (0, 0) band of $B^2\Sigma - A^2\Pi_{1/2}$ and (0, 0) and (1, 1) bands of $B^2\Sigma - A^2\Pi_{3/2}$ subsystems are found suitable for the analysis. The bands are red-degraded and double-headed. All the possible six branches could be traced out in all the three sub-bands. The J numbering to the branch lines could be assigned by comparing the combination differences

$$R_1(J) - P_1(J) = Q_{R_{12}}(J) - O_{P_{12}}(J)$$

and
$$R_2(J) - P_2(J) = S_{R_{21}}(J) - O_{P_{21}}(J)$$

for the 0th level of the $B^2\Sigma$ state in the two sub-bands. The combination differences thus calculated in the present analysis agree with each other but differ considerably from the combination differences reported by Chaudhary and Upadhyaya (1969) and by Barwald *et al* (1934) at higher J values where the spin splitting is resolved. However, they agree at lower J . It was found that even the combination differences $R_1(J) - P_1(J) = Q_{R_{12}}(J) - O_{P_{12}}(J)$ or the other, calculated using the data Barwald *et al* (1934) or Chaudhary and Upadhyaya (1969) do not match throughout the structure of band. The deviations are probably due to the incorrect identification of the main and satellite branches by Chaudhary and Upadhyaya (1969). A similar phenomenon observed in the analysis of B-X system by Barwald *et al* (1934) is discussed in § 3. The vacuum wave numbers and J assignments of the rotational lines in the three sub-bands are given in table 1.

The rotational constants were determined using a least squares fit computer program in which all the constants B' , B'' , D' , D'' , ν_0 , p'' and γ' were made free to vary simultaneously. Since the structure in (0, 0) band of both the subsystems shows perturbations, the data corresponding to the lines where the calculated and observed values differ by more than $\pm 0.1 \text{ cm}^{-1}$, were removed in the final fitting. It was found that the B'_0 value calculated from the two sub-bands was nearly the same. Therefore in the final fitting B'_0 value was kept fixed which reduced the errors in other constants appreciably. The molecular constants thus obtained along with the standard deviation of the fitting are given in table 2.

Table 1a. Vacuum wave number and J assignment of the rotational lines in $(0, 0)_{3/2}$ band of B-A system of CP.

J	$R_1(J)$	$Q_1(J)$	$P_1(J)$	$^S R_{21}(J)$	$^R Q_{21}(J)$	$^Q P_{21}(J)$
2.5						
3.5						
4.5						
5.5		22085.28				
6.5		84.25		22104.86		
7.5		83.21	22073.67	6.44		
8.5		82.06	71.19*	8.02		
9.5		80.91	68.67	9.55		
10.5		79.66	65.99	10.96		
11.5		78.39	63.43	12.45		
12.5		77.06	60.77*	13.81		
13.5		75.67	57.97	15.19		
14.5		74.25	55.15	16.49		
15.5	22094.41	72.76	52.34	17.74		22072.89
16.5	94.20	71.19*	49.47	18.89		71.19
17.5	95.05	69.60	46.53	20.04		69.74
18.5	93.78	67.94	43.51	21.07	22093.87	68.17
19.5	93.44	66.27	40.46	21.98	93.53	66.45
20.5	92.98	64.49	37.33	22.93	93.17	64.61
21.5	92.56	62.66	34.16	23.83	92.63	62.80
22.5	92.01	60.77*	30.92	24.67	92.20	60.88
23.5	91.37	58.87	27.62	25.55	91.60	59.09
24.5	90.76	56.91	24.29	26.19	90.96	57.11
25.5	90.01	54.80	20.90	26.80	90.28	55.04
26.5	89.17	52.69	17.42	27.42	89.57	52.99
27.5	88.31	50.60		27.95	88.71	50.60
28.5	87.44	48.32*		28.37	87.82	48.32*
29.5	86.58	46.02		28.75	86.88	46.30
30.5	85.71	43.63*			85.89	43.63*
31.5	84.65	41.14			84.85	41.46
32.5	83.49	38.70			83.66	39.00
33.5	82.39	36.11				36.37
34.5		33.45				33.64
35.5		30.68				

*refer to overlapping of lines.

3. Results and discussion

The molecular constants obtained from the present study have been compared with constants reported earlier in table 2. It is found that though the magnitude of the spin-splitting constant γ in the B state obtained here is the same as reported by previous workers, the sign is completely different. This is due to wrong identification of the main and satellite branches R_1 and $^R Q_{21}$ or Q_1 and $^Q P_{21}$; P_2 and $^P Q_{12}$ or Q_2 and $^Q R_{12}$ reported by the previous workers. This idea is strengthened by the comparison of the combination differences. If the order of the main and satellite branches in our analysis are interchanged the two combination differences do not agree at higher J . If the order of the main and satellite in the analysis

Table 1b. Vacuum wave number and J assignment of the rotational lines in $(1, 1)_{3/2}$ band of BA-System of CP

J	$R_1(J)$	$Q_1(J)$	$P_1(J)$	${}^R Q_{21}(J)$
0·5				
1·5		21863·45		
2·5		62·59		
3·5		61·72		
4·5		60·71	21855·47	
5·5		59·78	53·09	
6·5		58·69	50·59	
7·5		57·61	48·27	
8·5		56·49	45·70	
9·5		55·37	43·00	
10·5		54·00	40·56	
11·5		52·79	37·93	
12·5		51·36	35·17	
13·5		49·98	32·31	
14·5		48·46	29·62	
15·5		46·81		
16·5		45·21		
17·5		43·52		
18·5		41·75		
19·5		39·99		
20·5		38·22		
21·5		36·16		
22·5		34·37		
23·5	21864·49	32·30		21864·70
24·5	63·77	30·19		63·80
25·5	62·87			63·14
26·5	61·85			62·16

of Chaudhary and Upadhyaya (1969) are interchanged the two combination differences $R_1(J) - P_1(J) = {}^O R_{12}(J) - {}^O P_{12}(J)$ which did not agree initially match well. This agreement is achieved only on condition that we consider γ to be negative. A comparison of the γ value in the B-state of other isoelectronic molecules Co^+ , SiN , AlO , N_2^+ etc. supports our view.

Barwald *et al* (1934) who studied the rotational analysis of the B-X system have reported $\Delta\gamma = \gamma' - \gamma''$ to be $\sim 0.023 \text{ cm}^{-1}$. If we take our value of γ' to be correct the γ'' , value comes out to be -0.0305 cm^{-1} or $+0.0170 \text{ cm}^{-1}$. If we take $\gamma'' = -0.0305 \text{ cm}^{-1}$ the branch assignment of Barwald *et al* (1934) will be correct, however the constants B' , B'' , D' , D'' , ν_0 have to be changed to have a good reproduction of the branch lines. On the other hand if we take γ'' to be $+0.0170 \text{ cm}^{-1}$ only the assignment of R_1 and R_2 or P_1 and P_2 in the B-X system has to be interchanged. The same constants will reproduce the branch lines. A comparison of the spin splitting constant in the ground state of the isoelectronic molecules suggests that the γ value in the ground state of CP should be positive. This view suggests that the assignment of P_1 , P_2 or R_1 , R_2 branches in the B-X system should be interchanged.

Barwald *et al* (1934) studied the head-origin separation in the B-A system and reported that α_e , the vibration rotation interaction constant for the A-state was

Table 1c. Vacuum wave number and J assignment of the rotational lines in $(0, 0)_{1/2}$ band B-A system of CP

J	$R_2(J)$	$Q_2(J)$	$P_2(J)$	$Q_{R_{12}}(J)$	$P_{Q_{12}}(J)$	$O_{P_{12}}(J)$
0.5		21933.31				
1.5		33.96				
2.5		34.48	21930.96			
3.5		34.94	29.46			
4.5	21943.46	35.34*	28.44			21923.06
5.5	45.30	35.74	27.44*			20.66*
6.5	46.80	35.98	26.30*			18.26
7.5	48.28	36.12	25.09*			15.69
8.5	49.75		23.88*			13.04
9.5	51.10		22.66		21922.38	10.40
10.5	52.50		21.24*		21.24*	7.72
11.5	53.82		19.82		19.61	4.83
12.5	55.04		18.37		18.26	2.13
13.5	56.26		16.84		16.70	99.15
14.5	57.26		15.19	21935.59	15.08	96.10
15.5	58.40	35.34*	13.47	35.22	13.30	93.13*
16.5	59.31	35.07	11.79	34.84	11.69	90.15
17.5	60.16	34.64	9.96	34.39	9.80	86.92
18.5	60.98	34.07	8.12	33.87	9.99	83.59
19.5	61.70	33.51	6.22	33.31	6.01	80.33
20.5	62.48	32.87	4.14	32.58	4.01	77.05
21.5	63.04	32.12	1.97	31.85	1.90	
22.5	63.61	31.34	99.30	31.13	99.77	
23.5	64.05	30.46	97.71	30.26	97.51	
24.5	64.46	29.56	95.43	29.31	95.23	
25.5	64.75	28.53	93.13*	28.30	92.89	
26.5	65.15	27.44*	90.68	27.25	90.44	
27.5		26.30*	88.15	26.10	87.96	
28.5		25.09*	85.61	24.79	85.38	
29.5		23.88*	82.91	23.50	82.68	
30.5		22.50	80.26	22.38	79.94	
31.5		20.95	77.44	20.66*	77.28	
32.5		19.41	74.55	19.15	74.39	
33.5		17.80	71.27	17.45	70.85	

*refer to overlapping of lines.

0.0077 cm^{-1} . Subsequently, Huber and Herzberg (1979) using the same relation reported a value 0.0058 cm^{-1} . It is to be noted that the head-origin measurement gives an approximate value of α_e and a still better value can be obtained by rotational analysis. An analysis of $(1, 1)_{3/2}$ band enabled us to determine α -value in the A $^2\Pi_i$ state to be 0.00552 cm^{-1} which is very near the value given by Huber and Herzberg (1979) but much different from that of Barwald *et al* (1934). The α_e value in the A $^2\Pi_i$ state was also estimated using Peckeris relation ($\sim 0.0054 \text{ cm}^{-1}$). An agreement between the two values suggest that the potential energy curve of the A-state can be represented accurately by Morse potential function. The α_e value in the B $^2\Sigma^+$ state is also found slightly different from the value reported by previous workers. The most interesting aspect is the Λ -doubling value in the $^2\Pi_{1/2}$ state, which was found to be more than twice the value reported by Chaudhary and Upadhy (1969).

Table 2. Rotational constant for the B and A states of carbon monophosphide molecule (cm^{-1})

States	Constants	Our value	Value reported by Barwald <i>et al</i> (1934)	Value reported by Chaudhary and Upadhyaya (1969)
B ² Σ	B_0	0.68066 (±0.00000)		
	B_1	0.67282 (±0.00062)		
	B_e	0.68456 (±0.00062)	0.6829	0.67995**
	$D_e \times 10^6$	2.0 (±0.0)	1.82	...
	α_e	0.00784 (±0.00062)	0.00628	...
	r	-0.0073 (±0.0006)	0.006	0.0065
A ² Π _{3/2}	B_0	0.70642 (±0.00010)
	B_1	0.70089 (±0.00065)
	B_e	0.70917 (±0.00065)	...	0.70731
	$D_e \times 10^6$	1.18 (±0.13)	1.3	1.51
	α_e	0.00552 (±0.00065)	0.0077	...
	r	0.71303 (±0.00010)
A ² Π _{1/2}	B_e	0.71303** (±0.00010)	0.7135	0.712932**
	$D_e \times 10^6$	1.78 (±0.15)	1.3	0.40
	P	0.0093 (±0.0007)	...	0.0042
	Bands	Band Origin	Standard deviation of the fitting (SDV)	
	(0, 0) _{3/2}	22090.138 (±0.018)	(±0.047)	
	(1, 1) _{3/2}	21864.735 (±0.018)	(±0.062)	
	(0, 0) _{1/2}	21932.514 (±0.013)	(±0.054)	

The errors given in the parenthesis refer to our standard deviation (1σ) and not to our confidence limit.

**refers to B_0 value.

The standard deviation of fitting of the rotational lines, along with the error limits in different constants is given in table 2.

3.1 Perturbations

Perturbations have been observed at $N' = 9, 17, 24, 31$ and 34 in the rotational structure of the $(0, 0)$ band. The strength of perturbations is very weak and only either a small diffuseness or a slight shift (not measurable) in the rotational lines from their actual positions is observed. Perturbations are present at the same N values in both the sub-bands of the $(0, 0)$ band indicating that they occur in the $B^2\Sigma$ state. The nature of perturbations suggests that they are probably due to a $^2\Sigma - ^2\Pi$ (intermediate case). However the poor intensity of the rotational structure makes it difficult to draw any definite conclusion about the perturbations or the perturbing state.

3.2 Electron configuration

According to the molecular orbital theory the ground state of carbon monophosphide molecule can be given as

$$(Z\sigma)^2 (Y\sigma)^2 (\omega\pi)^4 (x\sigma) \dots ^2\Sigma^+;$$

the excited state $A^2\Pi_i$ arises due to the excitation of an electron from the bonding $(\omega\pi)^4$ orbital to bonding $(x\sigma)$ *i.e.*

$$(Z\sigma)^2 (Y\sigma)^2 (\omega\pi)^3 (x\sigma)^2 \dots ^2\Pi_i$$

The $B^2\Sigma$ state arises from the configuration

$$(Z\sigma)^2 (Y\sigma) (\omega\pi)^4 (x\sigma)^2 \dots ^2\Sigma^+$$

An estimate of dissociation energy in the A, B and X states using the relation $\omega_e^2/4\omega_e x_e$ supports that the A and the X states of this molecule dissociate into normal atoms $C(^3P) + P(^4S)$. The $B^2\Sigma$ state is expected to dissociate into $C(^3P) + P(^2D)$.

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