THE BAND SPECTRUM OF PHOSPHORUS PART I ROTATIONAL STRUCTURE

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ABSTRACT. The band spectrum of phosphorus, as excited in a discharge tube, has been photographed with a Hilger large quartz Littrow spectrograph and the bands (9,21), (5,21), (5,18) and (4,18) have been measured. The analysis of their rotational structure has led to the following values of the constants (in cms.$^{-1}$).

$B'_4=0.2346$ $B''_{18}=0.2799$
$B'_5=0.2323$ $B''_{21}=0.2736$
$B'_9=0.2255$

The constant for $v'=9$ agrees with that obtained by Herzberg and also by Ashley, the others being newly obtained. The absence of any perturbations in the rotational structure of the bands (5,21) and (5,18) has shown that the perturbations pointed out by Herzberg must be only vibrational.

INTRODUCTION

While the band spectrum of nitrogen has been very extensively studied, investigations on that of phosphorus are comparatively few. The P_2 molecule is well known to emit an extensive and typical band spectrum ranging from λ 3500 down to the very extreme ultraviolet till about λ1900. The lower region of emission does not appear to have been adequately investigated. Apart from the very early work, the more recent and important investigations on this band spectrum consist chiefly of those of Jakowlewa (1931), Herzberg (1932), Ashley (1933) and Jenkins (1935). Jakowlewa was the first to suggest the vibrational analysis of the spectrum. Herzberg confirmed and extended the vibrational analysis. He also reported the rotational structure of the bands with the initial levels $v'=8$, 9, 10, 11. The most important points in the work of Herzberg, however, were the detection of perturbation in the vibrational levels $v'=2$ and 5 and of the phenomenon of predissociation exhibited by the P_2 molecule.

Herzberg plotted the difference between the observed and the calculated $\nu(v',0)$ values against the vibrational quantum number v' and found the differences at $v'=2$ and 5 to be abnormal, and beyond what might be accounted for as possible errors of measurement. So he concluded that the vibrational levels $v'=2$ and 5 are strongly perturbed.

Ashley redetermined the rotational structure of the (8,27), (8,28), and (9,28) bands previously analysed by Herzberg and in addition, she made the fine structure analysis of the (6,22) and (6,23) bands lying further towards the ultraviolet. The bands were photographed in the second order of a 21-foot concave grating, a more accurate evaluation of the rotational constants being thereby obtained. The chief aim of her work was the estimation of the alternation ratio of the intensities of the rotational lines in the spectrum. A more direct method of determining this ratio was attempted later by Jenkins. The ratio arrived at was 3 : 1 within limits of experimental error in the case of (6,22), (9,28), (9,29) and (10,31) bands, while in the (5,21) band Jenkins got the ratio to be between 3.4 to 3.5 : 1. This larger ratio which is theoretically inadmissable was interpreted by him as due to strong perturbations in the band (5,21) or to another fainter band that may perhaps lie underneath this.

If the anomalous value is due to a strong perturbation it would be expected that similar anomalies might occur in other bands involving the vibrational level $v'=5$ which is reported by Herzberg to exhibit strong perturbations.

It is therefore found desirable to examine the rotational structure and determine the alternating intensity ratio in the case of bands having this perturbed vibrational level. The present part deals with the fine structure analysis of the (0,21), (5,21), (5,18) and (4,18) bands. Two of these have $v'=5$. The above four bands have been selected for study, as they are free from overlapping by other bands and, as such, are suitable for analysis even under the comparatively low dispersion used. The results of the determination of the intensities of the rotational lines and of the alternation ratio will be reported in a succeeding part.

EXPERIMENTAL

The phosphorus bands have been excited in an ordinary H-shaped discharge tube of the type used by Sastry (1941). Preliminary trials with tubes of different bore have shown that the bands could be excited conveniently in a tube with the central portion having a bore of about 2 mm. The container was filled with red phosphorus and the electrodes were aluminium rods. An uncondensed discharge from a 1/4 kilo-watt transformer was passed. It was found essential to heat the container frequently in order to get the spectrum free from nitrogen and other impurity bands. Overheating of the tube, however, had to be avoided as in such a case the discharge ceased to pass. The tube was continuously evacuated with a Hyvac pump which was protected from the phosphorus vapour by a series of absorbing towers containing potassium hydroxide, calcium chloride and ice-cooled buffers. Care was taken to see that phosphorus did not deposit itself on the quartz window by cooling the wider portion of the tube behind the window.

The instrument used for photographing the spectrum was the Hilger large quartz Littrow spectrograph of type EI, with a dispersion of 3.5 A.U. per mm. in the region investigated. With a very narrow slit width, exposures of about 30-40 minutes gave good photographs showing well-defined rotational structure.

ROTATIONAL CONSTANTS

TABLE I

Structure of the band (9,21)

J	R Branch	P Branch	$R(J)-P(J)$ $=\Delta_2F'$	$R(J-1)$ $-P(J+1)$ $=\Delta_2F''$	J	R Branch	P Branch	$R(J)-P(J)$ $=\Delta_2F'$	$R(J-1)$ $-P(J+1)$ $=\Delta_2F''$
29	35,788.0	35,760.7	27.3		53	708.8	660.1	48.7	58.1
30	785.2	758.1	27.1	33.3	54	702.6	653.0	49.6	58.4
31	783.2	754.7	28.4	33.4	55	699.8	650.4	49.4	59.5
32	780.2	751.8	28.4	35.1	56	694.7	643.1	51.7	60.3
33	777.6	748.0	29.6	34.9	57	690.9	639.5	51.4	63.4
34	775.6	745.3	30.3	36.7	58	683.0	631.3	51.7	63.2
35	772.0	740.9	31.1	38.8	59	681.0	627.7	53.3	63.8
36	769.7	736.8	32.9	38.3	60	673.2	619.2	54.0	65.2
37	767.0	733.7	33.3	—	61	670.7	615.8	54.9	65.4
38	763.7	—	—	41.6	62	663.0	607.8	55.2	66.7
39	760.7	725.4	35.3	42.6	63	660.1	604.0	56.1	69.5
40	758.1	721.1	37.0	43.8	64	—	593.5		
41	754.7	716.9	37.8	45.4	65	656.8			
42	751.8	712.7	39.1	45.9	66	646.2			
43	748.0	708.8	39.2	47.4	67	639.5			
44	745.3	704.4	40.9	48.2	68	635.7			
45	740.9	699.8	41.1	50.6	69	627.7			
46	736.8	694.7	42.1	50.0	70	624.8			
47	733.7	690.9	42.8	51.4	71	615.8			
48	—	685.3	—	52.7	72	609.3			
49	725.4	681.0	44.4	—	73	604.0			
50	719.3	673.2	46.1	54.7	74	601.4			
51	716.9	670.7	46.3	56.3	75	597.0			
52	711.1	663.0	48.0	56.8					

TABLE II

Structure of the band (5,21)

J	R Branch	P Branch	$R(J)-P(J)$ $=\Delta_2F'$	$R(J-1)$ $-P(J+1)$ $=\Delta_2E''$	J	R Branch	P Branch	$R(J)-P(J)$ $=\Delta_2F'$	$R(J-1)$ $-P(J+1)$ $=\Delta_2F''$
43	34,005.8				61	940.4	883.0	57.4	67.4
44	002.4			48.9	62	935.8	877.4	58.4	67.7
45	33,999.6	33,956.9	42.7	48.8	63	931.3	872.7	58.6	68.6
46	996.5	953.6	42.9	50.5	64	927.3	867.2	60.1	69.8
47	992.7	949.7	43.6	51.7	65	922.6	861.5	61.1	
48	989.7	944.8	44.9	52.3	66	918.3			
49	985.8	940.4	45.4	53.9	67	913.0			
50	—	935.8	—	54.5	68	908.2			
51	—	931.3	—	—	69	903.5			
52	—	927.3	—	—	70	899.2			
53	971.2	922.6	48.6	—	71	893.3			
54	968.6	918.3	50.3	58.2	72	888.5			
55	964.1	913.0	51.1	60.4	73	883.0			
56	—	908.2	—	60.6	74	877.4			
57	956.9	903.5	53.4	—	75	872.7			
58	953.6	899.2	54.4	63.6	76	867.2			
59	949.1	893.3	55.8	65.1	77	861.5			
60	944.8	888.5	56.3	66.1	78	856.5			

TABLE III

Structure of the band (5, 18)

	R Branch	P Branch	$R(J)-P(J) = \Delta_2F'$	$R(J-1) - P(J+1) = \Delta_2F''$	J	R Branch	P Branch	$R(J)-P(J) = \Delta_2F'$	$R(J-1) - P(J+1) = \Delta_2F''$
29	36,005.3	35,976.7	28.6	—	51	931.6	883.5	48.1	59.0
30	002.5	973.3	29.2	35.3	52	926.8	876.6	50.2	59.0
31	000.0	970.0	30.0	35.9	53	922.4	872.6	49.8	59.8
32	35,997.7	966.6	31.1	37.0	54	917.9	867.0	50.9	60.7
33	991.5	963.0	31.5	39.0	55	913.0	861.7	51.3	62.4
34	992.1	958.1	33.4	39.2	56	908.5	855.5	53.0	62.9
35	987.3	955.3	32.0	39.7	57	903.4	850.1	53.3	64.2
36	986.0	952.4	33.6	39.2	58	898.9	844.3	54.6	65.0
37	983.3	948.1	35.2	42.7	59	893.4	838.4	55.0	66.4
38	981.0	943.3	37.7	43.9	60	887.4	832.5	54.9	67.8
39	976.7	939.4	37.3	45.4	61	883.5	825.6	57.9	68.9
40	973.3	935.6	37.7	45.1	62	876.6	818.5	58.1	—
41	970.0	931.6	38.4	46.5	63	872.6	—	—	—
42	966.6	926.8	39.8	47.6	64	868.5	—	—	—
43	963.0	922.4	40.6	48.7	65	861.7	—	—	—
44	958.7	917.9	40.8	50.0	66	858.4	—	—	—
45	955.3	913.0	42.3	50.2	67	850.1	—	—	—
46	952.4	908.5	43.9	51.9	68	844.3	—	—	—
47	948.1	903.4	44.7	—	69	838.4	—	—	—
48	943.3	—	—	54.7	70	832.5	—	—	—
49	939.4	893.4	46.0	54.4	71	825.6	—	—	—
50	935.6	888.9	46.7	55.9	72	820.8	—	—	—

TABLE IV

Structure of the band (4, 18)

J	R Branch	P Branch	$R(J)-P(J) = \Delta_2F'$	$R(J-1) - P(J+1) = \Delta_2F''$	J	R Branch	P Branch	$R(J)-P(J) = \Delta_2F'$	$R(J-1) = P(J+1) = \Delta_2F''$
33	35,544.9	35,513.4	31.5	—	53	472.8	423.8	49.0	58.9
34	542.0	510.5	31.5	39.2	54	468.6	418.6	50.0	59.3
35	539.3	505.7	33.6	39.7	55	464.0	413.5	50.5	60.8
36	536.5	502.3	34.2	41.0	56	458.3	407.8	50.5	—
37	533.1	498.3	34.8	42.1	57	454.6	—	—	62.3
38	530.2	494.4	35.8	43.0	58	449.6	396.0	53.6	65.2
39	526.7	490.1	36.6	44.1	59	444.4	389.4	55.0	66.8
40	524.2	486.1	38.1	44.8	60	440.4	382.8	57.6	—
41	520.6	481.9	38.7	46.7	61	434.8	—	—	69.0
42	517.1	477.5	39.6	47.8	62	429.6	371.4	58.2	—
43	513.4	472.8	40.6	48.5	63	423.8	—	—	—
44	510.5	468.6	41.9	49.4	64	420.7	—	—	—
45	505.7	464.0	41.7	52.2	65	413.5	—	—	—
46	502.3	458.3	44.0	51.1	66	407.8	—	—	—
47	498.3	454.6	43.7	52.7	67	396.4	—	—	—
48	494.4	449.6	44.8	53.9	68	396.0	—	—	—
49	490.1	444.4	45.7	54.0	69	389.4	—	—	—
50	486.1	440.4	45.7	55.3	70	386.0	—	—	—
51	481.9	434.8	47.1	56.5	71	380.1	—	—	—
52	477.5	429.6	47.9	58.1	72	373.9	—	—	—

ROTATIONAL STRUCTURE

The phosphorus bands due to the P_2 molecule possess a simple rotational structure, the electronic transition involved being $^1\Sigma - {}^1\Sigma$. The predicted branches in a $^1\Sigma - \Sigma$ band are only a single P and a single R, the Q branch being forbidden. The fact that only the strong lines of the P branch need be assumed to be in coincidence with the strong lines of the R branch and similarly for the weak lines was of valuable help in deriving the analysis. The stronger lines are assigned odd values of J. In Tables I to IV the structure of the bands as divided into the R and P branches is given. These tables also contain combination differences. It is seen that the values of Δ_2F' agree for the (9,21) band and the (9,28) (*cf.* Ashley) justifying the assignment of a common initial vibrational level. Similarly, the agreement of Δ_2F'' values in the case of (4,18) and (5,18) bands confirms that the bands have a common final level. A difficulty is experienced during the analysis of the (5,21) band. At the tail end of the band, the assignment could be arrived at easily. But when the classification was extended towards the head of the band (beyond ν 33,956.9) the differences were found to be out of step. This at first suggested the existence of strong perturbations in this region. But, the analysis arrived at for the (5,18) band involving the level $v'=5$ extends very far towards the head of the band and does not show the definite existence of any perturbation. It is, therefore, considered that the difficulty in extending the analysis of the (5,21) band is due to the probable overlapping of a fainter band occurring just in this region. That this is plausible, is obvious from the photograph of the band also. Just after ν 33,056.9 there is seen in the picture a distinct change in the spectrum suggestive of an overlapping.

For determining the rotational constants the following formula for the second differences is used (*cf.* Jevon's Report on Band Spectra) :

$$\Delta_2F = 4B_v(J+\tfrac{1}{2}) + 8D_v(J+\tfrac{1}{2})^3.$$

The value of D_v was at first estimated from the usual relation $D_e = -\frac{4B_e^3}{\omega_e^2}$, in which ω_e was taken from the equation given by Herzberg and an approximate preliminary-value was adopted for B_e. Then the term $8D_v(J+\frac{1}{2})^2$ was subtracted algebraically from the corresponding $\Delta_2F/(J+\frac{1}{2})$. The resulting value of $4B_v$ obtained for different J values were then averaged. The absolute values of the combination differences were plotted against J in order to check the absolute numbering of the rotational quantum number. Only those points lying on the curve were taken for evaluating the constants. The procedure for the upper state as well as the lower was the same. Values of B_e and α are also calculated. The resulting constants are given in the following table which contains also those due to Herzberg and Ashley for comparison :

	$v''=21$	$v''=18$	$v'=9$	$v'=5$	$v'=4$
B $\mathrm{cm.}^{-1}$	0.2736	0.2799	0.2255	0.2323	0.2336

Author		Herzberg	Ashley
B_e'	0.2420	0.24197	0.2415
α'	0.0017	0.0017	0.00164
B_e''	0.3187	0.31424	0.3057
α''	0.0021	0.0019	0.00165

SUMMARY

The rotational structure of four bands, two of which involve the initial vibrational level $v'=5$, has been examined. The structure does not reveal any rotational perturbations and it is concluded that the perturbations shown by Herzberg must be only vibrational. The constants for $v'=4$, 5 and $v''=18$, 21 are newly obtained.

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