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Nuclear Spin of Phosphorus from Band Spectrum Analysis

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The emission spectrum of P_2 has been photographed in the first and second orders of the 21-foot grating. A strong alternation in intensity is observed in the successive rotational lines of many bands. The intensity ratio is found to be 3 : 1, hence the nuclear spin of phosphorus is $\frac{1}{2}(h/2\pi)$. A fine structure analysis was made of the (6,22), (6,23), in addition to the (8,27), (8,28) and (9,28) bands previously reported by Herzberg. Only P and R branches are present. The transition involved is ${}^1\Sigma\rightarrow{}^1\Sigma$. The odd levels of the ground state have the greater statistical weight. The following molecular constants are obtained; $Be'=0.2415$ cm^{-1}; $Be''=0.3058$ cm^{-1}; $\alpha'=0.00164$; $\alpha''=0.00165$.

INTRODUCTION

IN 1906 Geuter[1] observed the emission spectra of P_2 under low dispersion. Regularities in the band heads in the region from λ2690 to λ3577 were established. Several other band systems of "phosphorus" were also observed, several of which have been since identified as the emission spectra of other phosphorus compounds (PO, PH), the extended band system designated as "*C*" by Geuter being the only one due to P_2. He measured some individual lines of the band whose head is at 3246.72A on the Rowland system. This is the 9,29 band according to the present assignment of the quantum numbers. The lines near the head he estimated to be of constant intensity, whereas those further from the head were assigned alternating intensities of 2 : 1.

More recently Herzberg[2] has reported that the P_2 molecule showed the phenomenon of predissociation. From the emission spectrum he observed that the rotational lines of a band with a particular value of v' stop abruptly at a certain low rotational quantum number, the last few lines being still quite intense. Bands corresponding to higher values of v' are entirely missing, whereas in the case of bands with v' one unit lower, the lines run to a much higher rotational quantum number and then stop abruptly. From these phenomena Herzberg gave 5.5 volts as an upper limit to the heat of dissociation and stated that the absolute value of the predissociation limit could not be given since the origin of the system was not known. This was first definitely established by the work of Jakowlewa[3] on the fluorescence and absorption spectra of P_2. The assignment of vibrational quantum numbers adopted here is that given by Jakowlewa.

During the present investigation, an extensive article was published by Herzberg[4] dealing with the predissociation and its interpretation, and also with the rotational structure of certain bands. In previous correspondence with Dr. Herzberg, it had been decided that, to avoid duplication, the present work would not include the analysis of the bands of longest wave-length which show predissociation, but only the best resolved bands further to the ultraviolet which are suitable for a study of the alternating intensities. Data on the vibrational structure, showing marked perturbation of the levels $v'=2$ and 5 of the upper state, as well as a complete treatment of the predissociation, which leads to a value of 5.01 volts for the heat of dissociation of normal P_2, will be found in the article by Herzberg.

The principal purpose of the present work was the determination of the nuclear spin of the P atom from a consideration of the alternation of intensity[5, 6] in successive lines of a given branch of the rotational structure. At the beginning of the work, an analysis of the rotational structure

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[1] P. Geuter, Zeits. f. Wiss. Photographie **5**, 3 (1907).

[2] G. Herzberg, Nature **126**, 239 (1930).

[3] A. Jakowlewa, Zeits. f. Physik **69**, 548 (1931).

[4] G. Herzberg, Ann. d. Physik **15**, 677 (1932); Ergebnisse d. Naturwiss. **10**, 273 (1931).

[5] Jenkins and Ashley, Phys. Rev. **39**, 552 (1932).

[6] Jenkins and Ashley, Nature **129**, 829 (1932).

was made,[6] and it was shown to be that characteristic of a $^1\Sigma_u^+ \rightarrow {}^1\Sigma_g^+$ transition. Since the dispersion used here was superior to that available to Herzberg, the wave-number data for five bands, two of which are new, have been included below. The analysis has shown that the nuclei obey the Fermi-Dirac statistics, if the ground state is $^1\Sigma_g^+$ and that the previously estimated[6] alternation ratio of 3 : 1, requiring a nuclear spin of $\frac{1}{2}$, is certainly correct. The odd levels of the $^1\Sigma_g^+$ ground state have the greater statistical weight.

Analysis of the Bands

Because of the greater simplicity of absorption spectra over emission spectra, an attempt was first made to obtain the absorption spectrum of P_2 under high dispersion. This method would have the added advantage that one may measure the temperature of the absorbing gas and utilize the theoretical formulas for the intensity distribution in determining the ratio of alternating intensities, as done by Harvey and Jenkins.[7] These experiments were carried out by passing light from a H_2 discharge tube through a quartz tube 50 cm in length encased in an oven, the temperature of which could be raised to 1000°C. A side tube attached to the center of the absorption tube contained yellow phosphorus that had been three times distilled in vacuum. The pressure in the absorption tube could be regulated by varying the temperature of the phosphorus in the side tube. Under varying conditions of temperature and pressure only diffuse band heads were obtained, a continuous background of absorption being present even when the pressure was very low. The above phenomena may perhaps be attributed to the fact that P_2 shows predissociation.

Although the possibilities of this method were not exhausted, it was decided to determine if an alternation of intensity could easily be observed in the emission spectrum. The emission spectrum was obtained by passing an uncondensed discharge between aluminum electrodes through phosphorus vapor in a quartz tube. The pressure in the tube was maintained by vaporizing yellow phosphorus contained in a side tube into which it had been distilled in vacuum. In the later part of this work the red modification was used because of the greater ease of removing water vapor. The melting point of yellow phosphorus is 44°C. Red phosphorus sublimed at about 300°C, condensing as the yellow modification. The phosphorus vapor was dried with P_2O_5, and condensed three times before distillation into the quartz tube.

During passage of the discharge, red phosphorus was rapidly deposited on the walls of the tube and a very thin layer of this substance is very opaque to ultraviolet light. The window was kept clean by means of a flame. During the course of a run when all the yellow phosphorus was converted into red phosphorus, which has too low a vapor pressure to carry the discharge, it was readily reconverted by heating into the yellow form for another run. During runs in which the electrodes were kept fairly cool, a black electrically conducting deposit formed on the tube. This may have been aluminum phosphide.

The bands photographed, extending from $\lambda 2500$ to $\lambda 3500$, showed considerable overlapping of the rotational structure. Certain bands were, however, sufficiently open so that one might immediately say that they are singlet in nature. Only P and R branches are present, indicative of a $^1\Sigma \rightarrow {}^1\Sigma$ transition. A strong alternation in intensity was very apparent, particularly in the 6–22 band where the strong P lines are superimposed on the strong R lines. By inspection, it was possible to say with fair certainty that the alternation ratio was 3 : 1[6]; however other possibilities were eliminated later. Perturbations are very prominent in many bands, and will be made the subject of further study.

Since at the outset of this work nothing was known of the fine structure analysis, it was decided to make such an analysis of the (6,22), (6,23), (8,27), (8,28), (9,28) bands, primarily for the purpose of deciding whether the even or the odd levels have the greater statistical weight. Incidently the molecular constants were calculated from the corresponding bands.

Spectrograms used for analysis were taken in the first and second orders of a 21 foot concave grating. The 8,28 band was measured in the first order, while the other bands were measured in the second order. Fig. 1a shows the general appear-

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[7] Harvey and Jenkins, Phys. Rev. **35**, 789 (1930).

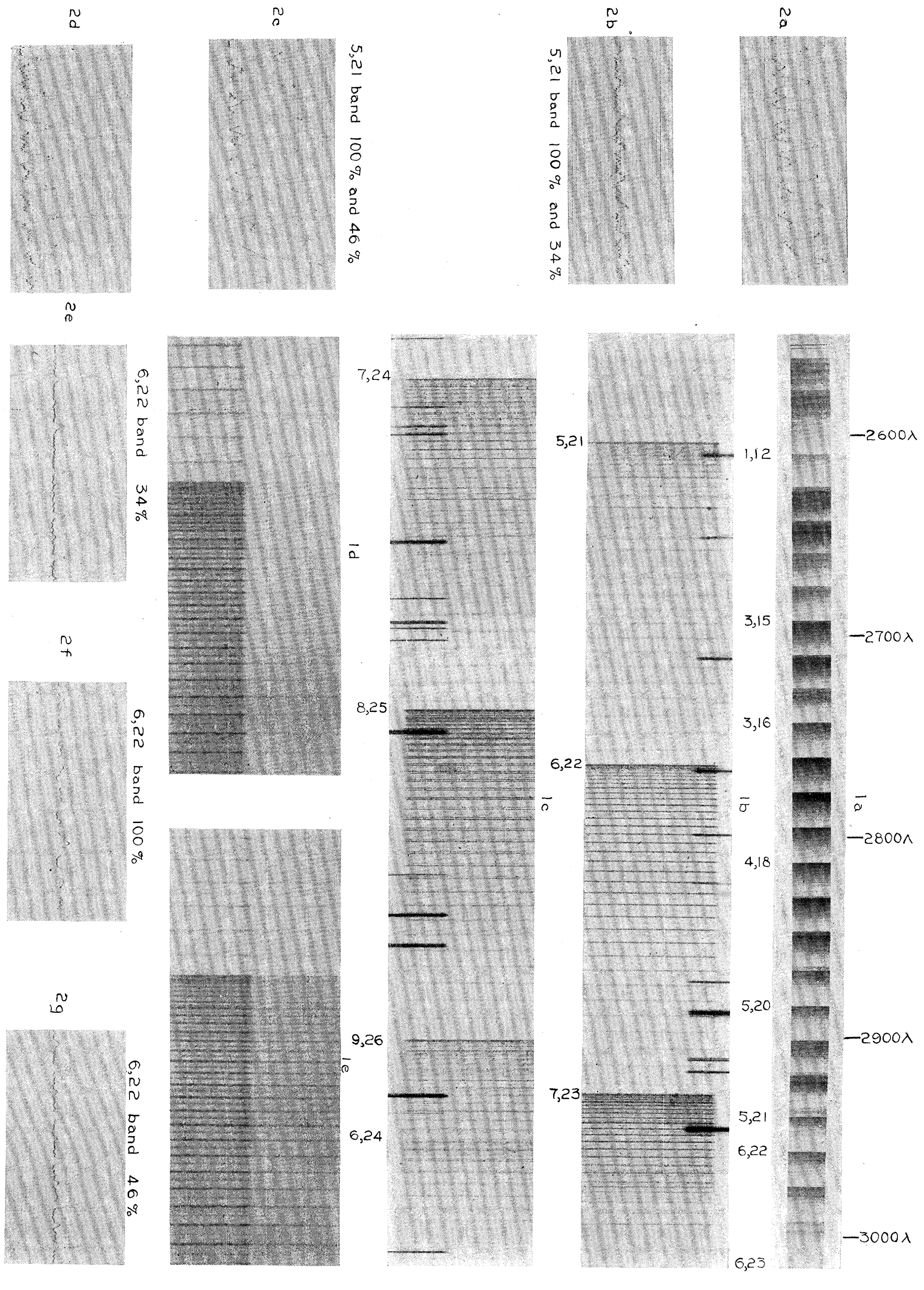

FIG. 1. Spectrograms of P_2 bands and their microphotometer analysis.

ance of the spectrum in its simpler part, while Figs. 1b and 1c show the spectrum in the region of the 6,22 and 8,25 bands respectively with greater enlargement. The dispersion is approximately 2.38A/mm for the first order and 1.27A/mm for the second order, in the regions studied. The wave-lengths given in *Transactions of the Astronomical Union*, Vol. III, 1929, and *Publications of the Allegheny Observatory*, Vol. VI, were used for the iron comparison lines. The strong lines could be measured with greater accuracy than the weak lines, the latter being necessarily omitted in measurements of some of the fainter bands. The lines of the 6,22 band were subject to error due to the superposition of the *P* and *R* branches.

It was easy to identify the *P* and *R* branches because of the greater intensity of the *R* branch near the head, the *P* branch increasing in relative intensity near the tail. When in doubt as to the identity of the branches from a superficial examination, the lines were microphotometered. The fact that only the strong lines of the *P* branch need be combined with the strong lines of the *R* branch and similarly for the weak lines, was of

TABLE I. *Bands of the* $\Sigma^1\rightarrow\Sigma^1$ *system. The lines of odd K value are the more intense.*

6,22 Band

K	R	P	Δ_2F'	Δ_2F''	K	R	P	Δ_2F'	Δ_2F''
17	33,841.82	33,825.82	16.00		46	33,784.28	33,741.51	42.77*	49.85*
18	33,840.87	33,823.97	16.90	19.72	47	33,781.14	33,737.47	43.67*	50.88*
19	33,839.91	33,822.10	17.81	20.82	48	33,777.90	33,733.40	44.50*	51.98*
20	33,838.87	33,820.05	18.82	21.89	49	33,774.66	33,729.16	45.50*	52.98*
21	33,837.70	33,818.02	19.68	22.99	50	33,771.27	33,724.92	46.35*	54.09*
22	33,836.53	33,815.88	20.65	24.04	51	33,767.84	33,720.57	47.27*	55.28*
23	33,835.17	33,813.66	21.51	25.07	52	33,764.35	33,715.99	48.36*	56.17*
24	33,833.97	33,811.46	22.51	26.09	53	33,760.70	33,711.67	59.03*	57.14*
25	33,832.45	33,809.08	23.37	27.41	54	33,756.97	33,707.21	49.76	58.29*
26	33,830.83	33,806.56	24.27	28.39	55	33,753.29	33,702.41	50.88*	59.32*
27	33,829.24	33,804.06	25.18	29.43	56	33,749.41	33,697.65	51.76*	60.49*
28	33,827.50	33,801.40	26.10	30.44	57	33,745.53	33,692.80	52.73*	61.57*
29	33,825.82	33,798.80	27.02	31.58	58	33,741.51	33,687.84	53.67*	62.64*
30	33,824.01	33,795.92	28.09	32.60	59	33,737.47	33,682.89	54.58*	63.53*
31	33,822.10	33,793.22	28.88	33.65	60	33,733.40	33,677.98	55.42*	64.82*
32	33,820.63	33,790.36	30.27	34.78	61	33,729.11	33,672.65	56.46*	66.05*
33	33,818.02	33,787.32	30.70	36.36	62	33,724.61	33,667.35	57.26	67.01*
34	33,815.88	33,784.27	31.61	36.88	63	33,720.19	33,662.10	58.09	
35	33,813.66	33,781.14	32.52	37.94	64	33,715.62			
36	33,811.46	33,777.94	33.52	39.00	65	33,711.06			
37	33,809.09	33,774.66	34.43	40.18*	66	33,706.52			
38	33,806.56	33,771.28	35.28	41.25*	67	33,701.53			
39	33,804.06	33,767.84	36.22	42.18	68	33,696.61			
40	33,801.40	33,764.38	37.02	43.36*	69	33,691.59			
41	33,798.80	33,760.70	38.10	44.43*	70	33,686.11			
42	33,795.92	33,756.97	38.95	45.51*	71	33,681.17			
43	33,793.22	33,753.29	39.93	46.51*	72	33,676.24			
44	33,790.36	33,749.41	40.95*	47.69*	73	33,670.55			
45	33,787.32	33,745.53	41.79*	48.85*					

6,23 Band

13	33,201.91	33,189.42	12.49		43	33,153.28	33,113.28	40.00*	46.76
14				15.47	44	33.150.52	33,109.47	41.05*	47.43*
15	33,200.70	33,186.44	14.26		45	33,147.65	33,105.85	41.80*	48.66
16				17.52	46	33,144.73	33,101.86	42.87*	49.51*
17	33,199.20	33,183.18	16.02		47	33,141.79	33,098.14	43.65*	50.63*
18	33,198.28	33,182.45	16.83	19.75	48	33,138.55	33,094.10	44.45*	51.70*
19	33,197.40	33,179.45	17.95	20.72	49	33,135.57	33,090.09	45.48*	52.60*
20	33,196.71	33,177.56	19.15	21.90	50	33,132.32	33.085.95	46.37*	53.77*
21	33,195.42	33,175.50	19.92	23.20	51	33,129.09	33,081.80	47.29*	54.80*
22	33,194.11	33,173.51	20.60	24.10	52	33,125.71	33,077.52	48.19*	55.86*
23	33,193.03	33,171.32	21.71	25.03	53	33,122.29	33,073.16	49.13*	56.88*
24	33,191.89	33,169.08	22.81	26.20	54	33,118.54	33,068.83	49.71	58.04*
25	33,190.30	33,166.83	23.47*	27.38	55	33,115.14	33,064.25	50.89*	
26	33,188.92	33,164.51	24.41*	28.18	56	33,111.50			60.14*
27	33,187.36	33.162.12	25.24*	29.33*	57	33,107.75	33,055.00	52.75*	61.16*
28	33,185.76	33,159.59	26.17*	30.38*	58	33,103.86	33.050.34	53.52*	62.22*
29	33,184.17	33,156.98	27.19*	31.41*	59	33,100.06	33,045.53	54.53*	63.29*
30	33,182.45	33,154.35	28.10*	32.55*	60	33,096.05	33,040.57	55.48*	64.75
31	33,180.64	33,151.62	29.02*	33.80	61	33,091.95	33,035.31	56.64	
32	33,178.73	33,148.65	30.08*	34.67*	62	33,087.87			
33	33,176.84	33,145.97	30.87*	35.81*	63	33,083.64			
34	33,174.81	33,142.92	31.89*	36.84*	64	33,079.10			
35	33,172.76	33,140.00	32.76*	37.94*	65	33,074.94			
36	33,170.65	33,136.87	33.78*	39.01*	66	33,070.48			
37	33,168.29	33,133.75	34.54*	39.94*	67	33,065.83			
38	33,165.73	33,130.71	35.02	41.07*	68				
39	33,163.60	33,127.22	36.38*	41.91	69	33,056.35			
40	33,161.01	33,123.82	37.19*	43.19*	70	33,051.37			
41	33,158.65	33,120.41	38.24*	44.14*	71	33,046.41			
42	33,156.23	33,116.87	39.36	45.37*	72	33,041.14			

TABLE I. (*Continued.*)

K	R	P	Δ_2F'	Δ_2F''	K	R	P	Δ_2F'	Δ_2F''
8,27 Band									
15	31,572.17	31,558.21	13.96		47	31,519.85	31,476.87	42.98*	49.46*
16				17.24	48	31,517.30	31,473.17	44.13	49.13
17	31,570.83	31,554.93	15.90		49	31,514.33	31,470.72	43.61	49.75
18				19.37	50	31,511.67	31,467.55	44.12	51.32
19	31,569.36	31,551.46	17.90		51	31,508.56	31,463.01	45.55	53.68*
20	31,568.54	31,550.27	18.27	21.46	52	31,505.40	31,457.99	47.51*	54.59*
21	31,567.57	31.547.90	19.67		53	31,502.39	31,453.97	48.42*	55.43*
22	31,566.59	31,546.06	20.53	23.44	54	31,499.37	31,449.97	49.40*	56.44*
23	31,565.52	31,544.13	21.39	24.63	55	31,495.95	31,445.95	50.00*	57.55*
24	31,564.40	31,541.96	22.44	25.52	56	31,492.62	31,441.82	50.80*	58.55*
25	31,563.20	31.540.00	23.20	26.57	57	31,489.31	31,437.40	51.91*	
26	31,561.78	31,537.83	23.95	27.59	58	31,485.67			60.68*
27	31,560.56	31,535.61	24.95		59	31,482.27	31,428.63	53.64*	61.46*
28				29.74	60	31,478.68	31,424.21	54.47	62.63*
29	31,557.71	31,530.82	26.89		61	31,474.80	31,419.64	55.16	
30	31,556.39	31,528.56	27.83	31.81	62	31,472.13			64.76
31	31,554.62	31,525.90	28.72	32.96	63	31,469.50	31,410.04	59.46	
32		31,523.43		33.91	64	31,465.81			
33	31,551.10	31,520.71	30.39*		65	31,461.84			
34	31,549.44	31,518.22	31.22*	35.81*	66	31,456.98			
35	31,547.41	31,515.29	32.12*	36.89	67	31,452.81			
36	31,545.38	31,512.55	32.83	37.91*	68	31,449.58			
37	31,543.52	31,509.50	34.02*	38.43	69	31,445.24			
38	31,541.53	31,506.95	34.58	39.97*	70	31,440.50			
39	31,539.35	31,503.55	35.80*	40.90*	71	31,436.24			
40	31,537.10	31,500.63	36.47	42.14*	72				
41	31,534.85	31,497.21	37.64*	43.00*	73	31,427.58			
42	31,532.29	31,494.10	38.19	44.10*	74	31,422.79			
43	31,530,11	31,490.75	39.36	45.22*	75	31,418.19			
44	31,527.67	31,487.07	40.60	46.24*	76				
45	31,525.13	31,483.87	41.26*	47.18*	77	31,408.56			
46	31,522.63	31,480.49	42.14*	48.26*					
8,28 Band									
19	30,959.07	30,941.33	17.74		41	30,926.90	30,889.09	37.81	42.83*
20	30,958.14			21.26	42	30,924.70	30,885.97	38.73	43.88*
21	30,957.40	30,937.81	19.59		43	30,922.45	30,883.02	39.43	45.12
22	30,956.38			23.27	44	30,920.28	30,879.58	40.70	45.91*
23	30,955.58	30,934.13	21.45		45	30,917.79	30,876.54	41.25	
24				25.32*	46	30,915.24			48.14*
25	30,953.33	30,930.26	23.07		47	30,912.73	30,869.65	43.08	
26				27.36*	48				
27	30,950.94	30,925.97	24.97		49	30,907.54			
28				29.54*	50	30,904.69			
29	30,948.20	30,921.40	26.80		51	30,901.91			
30	30,946.96	30,919.27	27.69	31.53*	52	30,899.21			
31	30,945.37	30,916.67	28.70	32.42	53	30,896.20			
32		30,914.54		33.70*	54	30,893.18			
33	30,942.13	30,911.67	30.46		55	30,890.26			
34	30,940.49	30,909.02	31.47	35.71*	56	30,886.94			
35	30,938.75	30,906.42	32.33	36.83*	57	30,884.00			
36	30,936.81	30,903.66	33.15	37.80*	58				
37	30,935.10	30,900.95	34.15	38.76*	59	30,877.40			
38	30,932.95	30,898.05	34.90	39.98	60	30,873.31			
39	30,931.19	30,895.12	36.07	40.79*	61	30,870.34			
40	30,928.80	30,892.16	36.64	42.10					
9,28 Band									
19	31,391.96	31,372.73	19.23		48	31,339.60	31,296.00	43.60*	50.04*
20	31,391.07	31,371.68	19.39	21.18	49	31,336.90	31,292.36	44.54*	51.00*
21	31,390.27	31,370.78	19.49	20.86	50	31,334.00	31,288.60	45.40*	52.12*
22	31,389.09	31,370.21	18.88	23.46	51	31,331.04	31,284.78	46.26*	53.11*
23	31,388.05	31,366.81	21.24	24.39	52	31,327.77	31,280.89	46.88	54.18*
24	31,387.07	31,364.70	22.37	25.41*	53	31,324.94	31,276.86	48.08*	
25	31,385.69	31,362.64	23.05*	26.68	54	31,321.80			56.16*
26	31,384.56	31,360.39	24.17	27.48*	55	31,318.55	31,268.78	49.77*	
27	31,383.11	31,358.21	24.90*	28.77	56				58.17*
28	31,381.91	31,355.79	26.12	29.57*	57	31,311.93	31,260.38	51.55*	
29	31,380.26	31,353.54	26.72*	30.80	58	31,308.49			60.20*
30	31,378.74	31,351.11	27.63*	31.63*	59	31,305.15	31,251.73	53.42*	
31	31,377.06	31,348.63	28.43*	32.71*	60	31,301.45			62.34*
32	31,375.15	31,346.03	29.12	33.61*	61	31,297.36	31,242.81	54.55	
33	31,373.62	31,343.45	30.17*	34.33	62	31,294.25			63.84
34	31,371.78	31,340.82	30.96	35.64*	63	31,290.12	31,233.52	56.60	
35	31,370.03	31,337.98	32.05*	36.61*	64	31,286.83			66.32
36	31,368.10	31,335.17	32.93*	37.78*	65	31,283.52	31,223.80	59.72	
37	31,366.05	31,332.25	33.80*	38.83*	66	31,279.13			
38	31,364.00	31,329.27	34.73*	39.80*	67	31.276.92			
39	31,361.88	31,326.25	35.63*	40.82*	68				
40	31,359.55	31,323.18	36.37*	41.86*	69	31,266.92			
41	31,357.33	31,320.02	37.31*	42.54	70				
42	31,355.00	31,317.01	37.99	43.80*	71	31,258.25			
43	31,352.58	31,313.53	39.05*	44.92*	72				
44	31,350.18	31,310.08	40.10*	45.88*	73	31,249.50			
45	31,347.63	31,306.70	40.93*	46.46	74				
46	31,345.03	31,303.72	41.31	47.93	75	31,240.48			
47	31,342.40	31,299.70	42.70*	49.03*					

aid in finding the correct combination relations. The numbering could have been found very directly from the bands which show predissociation. However, the bands which showed predissociation, *viz.*, the (10,29), (11,30), (10,30), and (11,31) bands, were less favorable for measurement from the standpoint of intensity and are expected to give irregular values of the band constants. Perturbations allowed a very definite verification of the correctness of the assignment of rotational quantum numbers, K, and of the resulting combination relations. The absolute values of the combination differences, $\Delta_2 F$, were plotted against K in order to check the absolute numbering of K. Table I gives the analysis of the five bands studied.

The following are the equations for the $\Delta_2 F$ values:

$$\Delta_2 F' = 4B_v'(K'+\tfrac{1}{2}) + 8D_v'(K'+\tfrac{1}{2})^3 + \cdots,$$

$$\Delta_2 F'' = 4B_v''(K''+\tfrac{1}{2}) + 8D_v''(K''+\tfrac{1}{2})^3 + \cdots.$$

One method for obtaining B_v from this equation, especially applicable when D_v is very small, is to write

$$4B_v = \Delta_2 F/(K+\tfrac{1}{2}) - 8D_v(K+\tfrac{1}{2})^2.$$

A preliminary value of B_v may be calculated by dividing $\Delta_2 F$ by $4(K+\frac{1}{2})$. This value may be used for calculating D_e in the equation $D_e = -(4B_e^3/\omega_e^2)$. The term $8D_v(K+\frac{1}{2})^2$ is to be subtracted algebraically from the corresponding $(\Delta_2 F''/(K+\frac{1}{2}))$. The resulting values of $4B_v$ obtained for different K values are then averaged. In this work the preliminary value of B_v'' was calculated with only the combination differences for even K values from 30 to 46. The values of ω_e were taken from the equation of Jakowlewa.[3] The variation of D_v with v is immaterial, owing to the smallness of D_v itself; hence D_e'' itself was used as the average value of D_v''. Only those values corresponding to $\Delta_2 F''$ indicated by an asterisk in the tables were used in calculating the final average values of $4B_v$. Other values were obviously irregular due to perturbations or doubtful measurements. The probable error in $4B_v''$ was calculated by least squares, giving equal weight to each point.

The procedure for the upper level was similar.

TABLE II. *Constants of P_2 molecule.*

	B cm^{-1}	Herzberg
$v''=22$	$0.2286_9 \pm 0.00006$	
$v\ =23$	$0.2671_5 \pm 0.00004$	
27	$0.2602_5 \pm 0.00008$	0.2606_9
28	$0.2590_1 \pm 0.00005$	0.2587_1
29		0.2566_8
30		0.2546_3
31		0.2529_5
32		0.2515_7
$v\ =\ 6$	$0.2309_1 \pm 0.00006$	
8	$0.2273_0 \pm 0.00007$	0.2274_6
9	$0.2260_6 \pm 0.00006$	0.2255_3
10		0.2239_0
11		0.2222_0
$B_e' \pm 0.2415_1 \pm 0.0007_4$		$B_e'' = 0.3057_9 \pm 0.0006_9$
$\alpha' = 0.00164 \pm 0.00009$		$\alpha'' = 0.00165 \pm 0.00003$
$r_e' = 2.12 \times 10^{-8}$ cm		$r_e'' = 1.88 \times 10^{-8}$ cm

The resulting constants with their probable errors are summarized in Table II, and the constants obtained by Herzberg[4] are included for comparison. A least squares solution was made of the equation $B_v = B_e - \alpha(v+\frac{1}{2})$ and the resulting values of B_e and α are also given in Table II, together with their probable errors calculated by external consistency.[8] The determination of the constants B_e evidently involves a considerable extrapolation. The probable errors given are based on a linear B_v curve, and are not a true measure of the error if their curve is not strictly linear, as is almost certainly true in the upper state. Herzberg[4] obtained the values $B_e' = 0.24197$, $\alpha' = 0.0017_2$, $B_e'' = 0.31424$, $\alpha'' = 0.0019_5$. The rather poor agreement with the value of Table II is principally due to the fact that the constants from the higher vibrational levels used by Herzberg show large irregularities, and do not fit a smooth curve within experimental error in either the upper or the lower states.

ALTERNATING INTENSITIES

Since the ratio of intensities of the strong to the weak lines in a given series was observed by inspection to be fairly large, a small value of the nuclear spin was indicated. The only values at all possible are $\frac{1}{2}$ and 1, corresponding to alternation ratios of 3 : 1 and 2 : 1 respectively.[9] However it would be unreasonable on the basis of other experimental evidence to assume that the phosphorus nucleus could have an even number of

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[8] R. Birge, Phys. Rev. **40**, 207 (1932).

[9] R. Mulliken, Rev. Mod. Phys. **3**, 149 (1931).

units of spin. A direct measurement of the alternation ratio was not attempted, but a method was devised which definitely distinguishes between the possible values of 3 : 1 and 2 : 1. For this purpose blackened wire screens of about 34 and 46 percent transmission were used. These screens, which were prepared and used according to the directions of Harrison,[10] were calibrated in the exact position which they were to occupy during the experiment. The light from an automobile headlight, placed at the position occupied by the phosphorus discharge tube, passed through a lens and then through the screen adjacent to the lens. The image of the filament was made to arrive somewhat out of focus on the open slit of the grating. This image extended beyond the edge of the slit so as to eliminate possible errors due to diffraction effects. One photronic cell of a Weston Illuminometer Model 603, placed back of the slit, received the transmitted light. The scale reading was taken several times with and without the screen in place. These screens are supposed to be neutral, and this neutrality in the visible region was checked by changing the voltage on the source.

The scale deflection of the illuminometer was checked by means of the inverse square law for linearity of response and was found to be accurate to within the limit of variation of the light source used, i.e., a fraction of a percent. The final average results of 16 measurements was 33.8 ± 0.5 percent for the first screen; 19 measurements for the second screen gave 45.9 ± 0.5 percent as a result.

The procedure in determining the alternation ratio was first to make an exposure of 10 minutes without the screens in the first, second, and third orders of the 21-foot grating, and then to make an exposure with the screens for the same length of time on the same plates immediately below the first exposure. This process was repeated until the total direct exposure was $1\frac{1}{2}$ hours and the exposure through the screen was for the same length of time. The current in the primary of the transformer was kept as constant as possible by regulating the pressure in the phosphorus tube. The repeated short exposures, 18 in all, switching from the direct to the screened, were carried out to obviate error due to possible variation in the source. Three runs were made, one with the 34 percent screen, the next with the 46 percent screen and the last a repetition with the 34 percent screen. The microphotometer curves of the direct exposures taken on different days on different plates but with similar conditions of development were surprisingly constant, and therefore the intermittent exposure process was possibly an unnecessary precaution.

Figs. 1d and 1e are enlargements of the 34 and 46 percent exposures, respectively, of the 6,22 band. If the alternation ratio were 2 : 1, one would expect the strong lines in the screened exposure of Fig. 1e to be slightly less intense than the weak lines in the direct exposure, and in Fig. 1d very much less intense. On the other hand, if the ratio is 3 : 1, the strong lines in the screened exposure of Fig. 1e should be considerably more intense than the weak lines in the direct exposure, while in Fig. 1d they should be practically equal. Inspection of these figures and of the microphotometer curves taken where the background is least shows that 2 : 1 is not possible, and that the results are closely those expected for 3 : 1. Figs. 2f, 2e and 2g show microphotometer curves for direct, 34 percent and 46 percent exposures of the 6,22 band. Only one direct exposure is included since the second one is a very close duplicate of the one shown. Figs. 2c and 2d show part of the 5,21 band for direct and 46 percent exposure. Figs. 2a and 2b show the 5,21 band for direct and 34 percent exposure.

The outstanding difficulty in this method is the effect of background, which was much heavier with the direct exposures. If there were no background and the intensity ratio is 3 : 1, the heavy lines of the 34 percent exposure should correspond closely in blackening to the weak lines of the direct exposure. Heavy lines of the 46 percent exposure are consistently heavier than the light lines taken directly. The heavy lines of the 34 percent plate compare very favorably with the light of the direct exposure in the 5,21 band, where the background is least marked. The 46 percent exposure in this case is much too heavy. For other bands with stronger background the 46 percent is too strong, but the 34 percent appears too light. The true ratio of the intensity of the heavy lines to that of the light lines midway

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[10] G. Harrison, J. Opt. Soc. Am. **18**, 493 (1929).

between is obviously the same for the direct exposure and for the 34 and 46 percent screens. However, the ratio of the heights of the microphotometer curve peaks of heavy to light lines was least for the direct exposure and greatest for the 34 percent exposure. Hence the background will have the effect of enhancing the light lines of the direct exposure to a greater extent than the heavy lines of the 34 percent or 46 percent exposure. Thus due to background, the light lines of the direct exposure may be expected to appear heavier than lines of equal intensity on a lighter background.

Another possible source of error is the following. Two adjacent lines may be entirely distinct for a light exposure, but if the exposure is heavy, the denser line of the two tends to raise the relative height of the intensity peak of the lighter line. This was obvious in the case of some of the microphotometer curves. This fact tends to make the intensity ratio appear less than it actually is.

Self-absorption in the P_2 vapor will also tend to increase the density of the light lines relative to the heavy lines. The column of discharge focussed on the slit of the grating was two inches long.

Now, as just noted, the observed apparent intensity ratio is closely 3 : 1 in the 5,21 band, where the background is the lightest. Moreover, the above sources of possible error all tend to give an observed intensity ratio slightly less than the true value, and in the remaining bands the observed ratio *is* slightly less than 3 : 1. We therefore conclude that the actual ratio of the strong to the weak lines is 3 : 1 within the limits of experimental error. It is certainly not 2 : 1.

Now it is known that the ratio of intensity of strong to weak lines for a homonuclear molecule is $(I+1)/I$, where I is the number of Bohr units of spin possessed by the nucleus. Hence the spin of the nucleus of the phosphorus atom is one-half a Bohr unit, i.e., $\frac{1}{2}(h/2\pi)$ erg sec.

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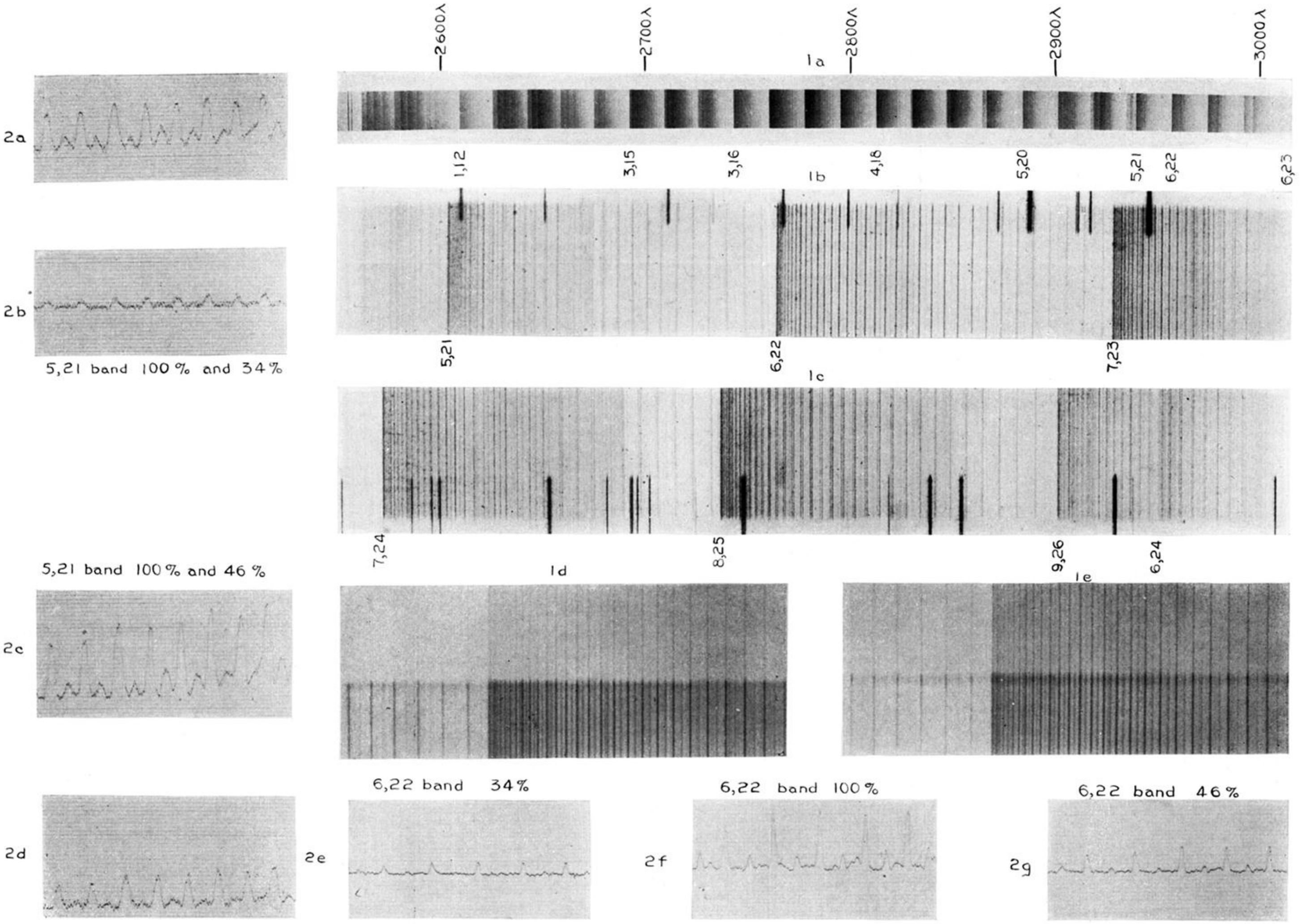

FIG. 1. Spectrograms of P_2 bands and their microphotometer analysis.