attempts of the electron avalanches to initiate the retrograde streamers which are the forerunners of negative point breakdown with larger points.¹³ They result from avalanches which would cause breakdown by positive streamers in a larger uniform gap. The streamers cannot advance all the way to the point cathode owing to the positive space charge which accumulates before the whole discharge is choked off. For still larger points the retrograde streamers reach the point and may cause breakdown.

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Zeeman Effect Data and Preliminary Classification of the Spark Spectrum of Praseodymium—Pr II

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The Zeeman effect of praseodymium has been studied at fields up to 95,000 oersteds over the range 2400 to 7100A. g and J values have been determined for 74 Pr II levels from resolved Zeeman patterns of 141 lines. With these data, together with new wave-length data from the M.I.T.-W.P.A. Wavelength Project which have been applied to the spectroscopic interval sorter and interval recorder, a quadratic term array has been set up which accounts for 312 lines. This array is consistent with King's temperature classification of the lines and with all previous hyperfine structure observations. It is self-consistent in g values to an average deviation of 0.005 unit, and in wave numbers to an average deviation of 0.08 cm⁻¹. Previously published hyperfine structure measurements were found insufficiently precise to aid the classification, but were of value in its verification. The lowest term of Pr II is found to be $f^{3}({}^{4}I^{o}) \cdot s - {}^{5}I^{o}_{4}$. Most of the strong lines showing hyperfine structure arise from the $f^{3}s$ configuration.

THE spectra of praseodymium have long defied classification, both because of the complexity of this rare-earth atom, and because many of its lines show hyperfine structure difficult to measure. White¹ has published extensive and valuable data on the hyperfine structure of Pr II, but these prove to be not quite precise enough to establish a classification.

The M.I.T. Wavelength Tables² list 2708 strong lines of praseodymium, and the unpublished W.P.A. card catalog at M.I.T. contains 3454 lines of all intensities assigned to the element. Actually the spectrum is so rich that the number of observable lines is limited only by the difficulty of distinguishing true lines from bands. The available description of the spectrum between 8000 and 2400A is fairly good, though limited in wave-length precision by the difficulties of measurement introduced by partially resolved hyperfine structure patterns (h.f.s.). Unless wave-length values accurate to ± 0.003 A can be obtained, it is impossible in so complex a spectrum to determine which is the correct quadratic array of the many obtained from the combination

TABLE I. Fields for various spectrograms.

| Set No. | FIELD | SET NO. | FIELD |
|----------------|------------------|--------------|------------------|
| Z 41 H | 95,000 oersteds | Z 47 | 89,900 oersteds |
| Z 41 L Z 42 | 72,340 90.860 | Z 48 Z 63 | 87,400 89,290 |
| Z 44 | 91,500 | Z 73 | 87,540 |
| Z 45 Z 46 | 91,500 86,400 | | 85,510 87,970 |

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¹³ L. B. Loeb and J. M. Meek, *Mechanism of the Electrical Spark* (Stanford Press, 1941), pp. 82, 87, 99, 170.

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¹ H. E. White, Phys. Rev. **34**, 1397 (1929).

² (John Wiley and Sons, New York, 1939.)

principle with the interval sorter³ and recorder.⁴ In the absence of data of suitable precision regarding wave-length and h.f.s., Zeeman effect measurements appeared to give the most powerful method of attacking the classification of the Pr spectra.

No Zeeman effect measurements on Pr lines appear to have been made hitherto, probably because of the high magnetic and spectrographic resolution needed for lines showing h.f.s. The availability of fields approaching 100,000 oersteds,⁵ combined with spectrographs of high dispersion capable of giving Zeeman exposures in a few minutes, has now made possible the resolution of many patterns. The data thus obtained gave the desired start on the classification, which was then verified and extended by wave-length, h.f.s., and temperature class data.

The three concave gratings and other apparatus used have been described in previous papers dealing with the spectra of other elements.6,7 An arc carrying 4 amp. was run between electrodes of silver containing 20 percent of powdered praseodymium chloride. The arc so obtained was the brightest and steadiest we have yet produced in a strong magnetic field with any element, but most of the lines emitted were found to belong to Pr II and Pr III. Eleven sets of spectrograms were obtained, at fields listed in Table I. Each set contained p, n, and no-field exposures on each of from 12 to 24 plates 20 inches long, distributed throughout the spectrum.

All spectrograms were measured in both directions with an automatic comparator,8 and were reduced by W.P.A. clerical workers, who have been of great assistance in reading, recording, and averaging the measurements used in calculating the data which follow. The field intensities given in Table I were calculated from measurements on the raies ultimes of silver, copper, and calcium, and are believed to be correct to within ± 0.3 percent.



FIG. 1. Lowest terms of Pr II, showing alternate inverted and normal hyperfine-structure multiple terms in pairs.

Results

Table II contains the lines of Pr II which we have classified thus far with reasonable assurance. The wave-lengths in angstroms given in the first column have been taken from the M.I.T.Wavelength Catalogs, as have the arc intensities in the second column. The third column gives the temperature class, while the fourth gives the h.f.s. of the line according to White,¹ or in cases marked a, from King.⁹ v and r in this column indicate shaded toward short and long wavelengths, respectively. The next column contains the observed wave number, while the column headed o-c gives the difference, in 0.01 cm⁻¹ units, between the observed wave nunber and that calculated from the difference between the finally assigned wave numbers of the parent levels. The column headed "Comb." gives the lower and upper terms which appear to produce the line. This is followed by two columns giving the g values for these lower and upper levels as deduced from the observed patterns of the line where these could be interpreted.

 ³ G. R. Harrison, Rev. Sci. Inst. 4, 581 (1933).
 ⁴ G. R. Harrison, J. Opt. Soc. Am. 28, 290 (1938).
 ⁵ G. R. Harrison and F. Bitter, Phys. Rev. 57, 15 (1940).
 ⁶ G. R. Harrison and J. Rand McNally, Jr., Phys. Rev. 702 (1940). 58, 703 (1940).

J. P. Molnar and W. J. Hitchcock, J. Opt. Soc. Am. 11, 523 (1940).

⁸ G. R. Harrison, J. Opt. Soc. Am. **25**, 169 (1935); Rev. Sci. Inst. **9**, 15 (1938); G. R. Harrison and J. P. Molnar, J. Opt. Soc. Am. 30, 343 (1940).

⁹ A. S. King, Astrophys. J. 68, 194 (1928).

| TABLE I | Ι. | Pr | Π | Lines. |
|---------|----|----|---|--------|
|---------|----|----|---|--------|

| λ | I | CLASS H.F.S. | σ OBS. | 0-c | Сомв. | ÿ1 | g 2 | λ | I | CLASS H.F.S. | σ OBS. | 0-c | Сомв. | <i>g</i> 1 | g 2 |
|--|---|--------------|---|--|--|----|-----|--|---|--|--|--|---|------------|------------|
| 7099.54 7021.54 6850.55 6554.632 6454.865 6554.632 6475.287 6454.865 6397.996 6305.262 6292.639 6242.539 6244.344 6205.723 5062.539 6141.508 6025.723 5967.837 5892.231 5879.253 5813.593 5831.895 5563.93 5685.11 5581.895 5564.764 5637.36 5583.89 5571.9 5583.185 5583.99 5571.841 55560.21 5551.841 5550.20 5531.232 5531.841 5550.21 5531.841 5551.841 5551.841 5551.841 5552.27 5531.841 5552.373 5531.423 5531.423 5531.423 5531.423 5531.423 5531.423 5531.423 5531.423 5531.423 5531.423 5531.433 5522.773 5331.433 5522.773 5331.433 5522.773 5331.433 5522.713 5228.837 5331.433 5321.935 5311.119 5308.96 5321.67,61 5321.073 5292.630 5292.633 5292.6 | $\begin{array}{c} 2 & 6 \\ 4 & 10 \\ 3 & 3 \\ 3 & 12 \\ 9 & 9 \\ 9 \\ 10 \\ 5 \\ 12 \\ 5 \\ 5 \\ 0 \\ 3 \\ 6 \\ 2 \\ 5 \\ 5 \\ 1 \\ 10 \\ 2 \\ 4 \\ 8 \\ 8 \\ 1 \\ 4 \\ 1 \\ 4 \\ 8 \\ 8 \\ 1 \\ 4 \\ 1 \\ 4 \\ 8 \\ 8 \\ 1 \\ 4 \\ 1 \\ 3 \\ 7 \\ 3 \\ 2 \\ 2 \\ 2 \\ 2 \\ 10 \\ 1 \\ 2 \\ 2 \\ 2 \\ 2 \\ 2 \\ 2 \\ 2 \\ 2 \\ 5 \\ 0 \\ 2 \\ 2 \\ 2 \\ 5 \\ 0 \\ 0 \\ 4 \\ 8 \\ 5 \\ 0 \\ 3 \\ 4 \\ 8 \\ 5 \\ 1 \\ 1 \\ 2 \\ 2 \\ 2 \\ 5 \\ 0 \\ 0 \\ 1 \\ 0 \\ 2 \\ 2 \\ 2 \\ 5 \\ 0 \\ 0 \\ 1 \\ 0 \\ 1 \\ 0 \\ 2 \\ 2 \\ 2 \\ 2 \\ 1 \\ 0 \\ 0$ | V | $\begin{array}{c} 14081.54\\ 14287.97\\ 14287.97\\ 14583.55\\ 15228.95\\ 15439.07\\ 15487.75\\ 15625.58\\ 15963.56\\ 16010.08\\ 16181.40\\ 16121.64\\ 16223.615\\ 16225.15\\ 1625.16\\ 16121.40\\ 16121.64\\ 16223.615\\ 16225.15\\ 16225.15\\ 16225.15\\ 16225.15\\ 16225.15\\ 16225.15\\ 16225.15\\ 17004.26\\ 171064.26\\ 171064.20\\ 17205.10\\ 17572.35\\ 17577.35\\ 17577.35\\ 17577.35\\ 17572.35\\ 17577.35\\ 17572.35\\ 17572.35\\ 17573.64\\ 17741.48\\ 17741.54\\ 17741.54\\ 17741.90.81\\ 17909.52\\ 18009.52\\ 18032.95\\ 18032.95\\ 18032.95\\ 1802.18\\ 18473.85\\ 18578.53\\ 18588.53\\ 1858$ | 8313126211311205393513021110018021110018025817144700293142293142621320511520070777110340113040113031221541101293144213205115200511520070777110340113031011221154110111111111111111111111111111 | $\begin{array}{l} b^{3}l^{5}s^{-} = 3s\\ a^{3}H^{5}s^{-} = 8s\\ b^{3}l^{2}t^{-} = 2s\\ b^{3}l^{2}s^{-} = 17s\\ b^{3}l^{2}s^{-} = 17s\\ b^{3}l^{2}s^{-} = 2s\\ b^{3}l^{2}s^{$ | | | 5064.84 5060.40 5034.415 5015.543 5010.454 5002.454 4991.774 4991.774 4991.774 4991.774 4991.774 4991.774 4991.774 4991.774 4991.774 4991.28 4992.630 4912.629 4901.483 4912.629 4901.483 4912.629 4901.483 4912.629 4901.483 4876.257 4856.038 4877.81 4876.257 4856.038 4839.540 4826.649 4826.649 4826.649 4826.649 4826.649 4826.649 4826.649 4826.649 4826.649 4826.649 4826.649 4778.303 4766.906 4766.322 4765.222 4765.2227 4765.2227 4765.2227 4766.354 4778.303 4766.906 4766.322 4766.322 4766.322 4765.2227 4765.2227 4765.2227 4768.354 4778.303 4766.906 4768.354 4778.303 4766.906 4768.354 4778.303 4766.906 4766.322 4765.2227 4765.2227 4765.2227 4765.2227 4765.2227 4765.2227 4765.227 4766.355 4746.355 4746.355 4746.355 4746.355 4746.355 4746.355 4746.355 4746.355.87 4767.408 4679.112 4678.139 4668.454 4679.412 4678.139 4668.454 4679.408 4674.635 4774.635 4570.565 4560.665 4570.565 4560.066 4570.565 4560.066 4570.565 4560.066 4570.565 4560.066 4570.565 4560.066 4570.565 4560.066 4570.565 4560.066 4570.565 4560.066 4570.565 4560.066 4570.565 4560.066 4570.565 4560.066 4570.565 4560.066 4570.565 4560.222 4560.222 4560.237 4560.237 4560.237 4560.237 4560.237 4560.237 4560.237 4560.237 4560.237 4560.237 4560.237 4570.2575 4500.066 4570.565 4500.066 4570.429 4500.066 4570.429 4500.066 4570.429 4500.066 4570.429 4500.066 4570.429 4500.066 4570.429 4500.066 4570.429 4500.066 4570.429 4500.066 4570.429 4500.429 4500.429 4500.429 4500.429 4500.429 4500.429 4500.429 4500.429 4500.429 4500.429 4500.429 4500.429 4500.429 4500.429 4500.429 4500.429 4500.429 4500.429 4500.429 | $\begin{array}{c} 2\hbar\\ 1\\ 2\\ 30\\ 4\\ 2\\ 5\\ 8\\ 3\\ \frac{2}{h}\\ 4\\ 1\\ 40\\ 3\\ 10\\ 5\\ 20\\ 0\\ 40\\ 40\\ 25\\ 8\\ 3\\ \frac{2}{h}\\ 4\\ 1\\ 40\\ 3\\ 10\\ 5\\ 20\\ 30\\ 40\\ 25\\ 8\\ 4\\ 5\\ 2\\ 8\\ 12\\ 3\\ 10\\ 6\\ 10\\ 105\\ 200\\ 10\\ 5\\ 125\\ 12$ | $\begin{array}{c c c c c c c c c c c c c c c c c c c $ | 19738.47 19751.50 19755.79 19857.76 19975.150 19975.150 19975.150 19975.150 19982.48 19941.79 19976.143 19984.63 20027.39 20027.39 20027.39 20027.39 20027.20 20110.35 20122.22 20342.63 20350.63 20450.53 20450.50 20459.79 20450.50 20459.79 20450.50 20459.79 20450.50 20574.48 20567.47 20742.54 20742.54 20751.26 20574.48 20657.37 20459.50 20459.5 | $\begin{array}{c} 224457759132188088772441076107741318115020462677743668361414120113145333444024444614421194123501100855813392010131111561921111111111111111111111111111111$ | $\begin{array}{c} a^{3}I^{*}a = 6a\\ b^{3}I^{*}a = 2b;\\ a^{3}I^{*}a = 1b;\\ a^{5}I^{*}a = 1b;\\ a^{5}I^{*}a = 1b;\\ a^{5}I^{*}a = 2b;\\ a^{5}I^$ | | |

TABLE II.—Continued.

| λ | I | CLASS 1 | H.F.S. | σ OBS. | 0-c | Сомв. | Ø1 | <i>0</i> .» | <u>></u> | I | CLASS | HES | σ 0BS | 0-0 | Сомв | <i></i> | <i>П</i> а |
|-----------------------------------|---|------------------------|------------------|----------------------------------|------------------------------|---|-----------------------------|---------------------------|----------------------------------|---|-------------------------|------------------|------------------------------------|------------------------|---|-------------------------------|---------------------------|
| 4493.119 4492.427 4487.821 | 25 25 40 | V e | 6v 6r 6v | 22250.03 22253.45 22276.29 | -18 -5 -8 | $a^{5}I^{\circ}_{7} - 15_{7}$ $a^{3}I^{\circ}_{6} - z^{5}I_{6}$ $a^{5}I^{\circ}_{5} - 4_{6}$ | | 9 | 4164.192 4161.65 4148.457 | 200 8 15 | III | 6v | 24007.52 24022.18 24098.59 | -9 + 1 + 2 | $a^{5}I^{\circ}_{6} - z^{5}I_{6}$ $a^{3}I^{\circ}_{6} - 297$ $a^{3}I^{\circ}_{6} - 18-$ | 0 86? | 92 |
| 4479.618 4477.259 | 35 125 | ĪV e | 6v | 22317.09 22328.85 | $^{+16}_{+8}$ | $a^5 L^{\circ_7} - 29_7$ $a^5 I^{\circ_6} - 11_6$ | 1.054 | 1.150 | 4143.136 4141.257 | 200 150 | III III | 6v 6v | 24129.52 24140.47 | -5 - 16 | $a^{5}I^{\circ}_{7} - z^{5}K_{8}$ $a^{5}I^{\circ}_{8} - z^{3}I_{7}$ | (1.177) 1.242 | 1.011 1.141 1.172 |
| 4473.835 4468.712 4458.336 | 30 125 90 | III e | 6 <i>r</i> 6v | 22345.93 22371.56 22423.62 | -5 -20 -12 | $a^{3}I^{\circ}_{5} - 2^{5}K_{6}$ $a^{5}I^{\circ}_{8} - 2^{5}K_{7}$ | 0.864 (1.250) | 0.963 1.125 | 4132.230 4118.481 4111.871 | 15 250 30 | | 6va 6v 5a | $24193.21 \\ 24273.97 \\ 24312.99$ | $^{+1}_{-15}$ | $a^{5}I^{\circ}_{6} - 18_{5}$ $a^{5}I^{\circ}_{5} - z^{5}I_{5}$ $a^{5}I^{\circ}_{4} - 12_{4}$ | (0.875) | 0.920 |
| 4454.382 4449.867 | 60 125 | | 6v 6v | 22443.52 22466.30 | $-10 \\ -10$ | $a^{5}I^{\circ}_{5} - 5_{5}$ $a^{5}I^{\circ}_{6} - z^{5}K_{6}$ | 1.075 | 0.961 | 4100.746 4100.22 | 200 15 | îi ê | 6v | 24378.94 24382.08 | -1 + 1 | $a^{5}I^{\circ}_{8} - z^{5}K_{9}$ $a^{5}I^{\circ}_{7} - 27_{6}$ | 1.256 | 1.221 |
| 4429.238 4429.238 4421.231 | 100 100 | III e | or 6v 6v | 22570.93 22570.93 22611.80 | $^{-45}_{+14}$ + 5 | $a^{5}I^{\circ}_{4} - 3_{5}$ $a^{5}I^{\circ}_{7} - 2^{5}K_{7}$ $a^{5}I^{\circ}_{7} - 17_{6}$ | (1.177) 1.175 | $1.165 \\ 1.061 \\ 1.110$ | 4096.822 4091.686 4081.018 | 30 50 50 | m e | 6?r?a | 24402.30 24432.93 24496 80 | -2 + 7 -16 | $a^{3}I^{\circ}{}_{5} - 19_{5}$ $a^{3}I^{\circ}{}_{5} - 20_{6}$ $a^{5}I^{\circ}{}_{6} - 19_{5}$ | 0.858 | 1.024 |
| 4413.765 | 90 50 | | Bra 6v | 22650.05 22658.31 | 0 | $a^{3}I^{\circ}{}_{5} - z^{3}K_{6}$ $a^{5}I^{\circ}{}_{7} - z^{5}I_{6}$ | 0.860 (1.177) | 0.992 1.046 | 4075.917 4073.305 | 15d 9 | = | | 24527.46 24543.18 | $-\frac{4}{-3}$ | $a^{5}I^{\circ}_{6} - 20_{6}$ $a^{3}I^{\circ}_{5} - 21_{5}$ | (1.004) | |
| 4405.849 4403.605 | 125 100 100 | IV e | ər Əv 6r | 22675.34 22690.75 22702.31 | -6 -4 -3 | $a^{5}I^{\circ}_{8} - z^{5}K_{8}$ $a^{5}I^{\circ}_{8} - z^{5}K_{8}$ $a^{3}I^{\circ}_{7} - 30_{8}$ | 0.605 (1.250) | 0.823 | 4062.817 4061.336 4056.543 | 150 4 100 | | 6r 6r | $24606.54 \\ 24615.51 \\ 24644.60$ | -5 + 4 + 8 | $a^{3}I^{\circ}_{6} - z^{3}K_{7}$ $a^{5}L^{\circ}_{7} - z^{3}K_{8}$ $a^{3}I^{\circ}_{7} - z^{3}K_{8}$ | (1 143) | 1.106 |
| 4395.788 4372.385 | 30 10 | V III e | | 22742.68 22864.41 | -17 + 6 | $a^{3}I^{\circ}_{6} - 19_{5}$ $a^{5}K^{\circ}_{5} - z^{3}H_{6}$ | 1.052 | (1.025) | 4054.845 4044.818 | 50 50 | | 6r 6ra | $24654.92 \\ 24716.03$ | $+12 \\ -3$ | $a^{3}I^{\circ}_{5} - 22_{6}$ $a^{5}I^{\circ}_{4} - z^{5}I_{5}$ | 0.862 0.605 | 0.991 0.910 |
| 4365.328 4359.795 | 125 6 100 | IV e | 3r | 22901.37 22930.43 | $^{+9}_{+2}$ $^{+3}_{+3}$ | $a^{5}L^{\circ}_{7} - z^{3}K_{7}$ $a^{5}L^{\circ}_{7} - z^{3}K_{7}$ | (1.143) | 0.994 | 4039.357 4038.467 4034.30 | $ \begin{array}{r} 50 \\ 15 \\ 20 \end{array} $ | | 6v 6?ra 6r | 24749.45 24754.91 24780.47 | $^{+1}_{-2}_{+16}$ | $a^{5}I^{\circ}_{6} - 22e$ $a^{5}I^{\circ}_{4} - 124$ $a^{3}I^{\circ}_{5} - 24e^{2}_{6}$ | 1.08 0.613 | 0.98 |
| 4352.752 4351.849 4347.490 | 4 80 | III e | Br Br | 22967.54 22972.30 22005.22 | $^{+9}_{-11}$ | $a^{5}L^{\circ}_{6} - z^{5}I_{7}$ $a^{3}I^{\circ}_{5} - z^{5}I_{5}$ | (0.860) | 0.904 | 4033.857 4031.755 | 50 50 | | 6v 6v | 24783.19 24796.11 | -15 + 6 | $a^5I^{\circ}_7 - 30_8$ $a^5I^{\circ}_6 - 23_7$ | (1.177) (1.064) | 1.077 1.089 |
| 4338.694 4333.913 | 100 150 | IV e | 57 57 3v | 23041.98 23067.37 | $^{+4}_{+32}$ | $a^{5}I^{\circ}_{6} - 23_{7}$ $a^{5}I^{\circ}_{6} - z^{5}I_{5}$ | (1.037) 1.062 | (0.990) 1.075 0.910 | 4015.389 4008.714 4000.190 | 50 150 50 | | 61ra 6r 6v | 24897.18 24938.64 24991.77 | $^{+1}_{-14}$ | $a^{3}I^{\circ}_{5} - 25_{5}$ $a^{3}I^{\circ}_{7} - z^{5}H_{7}$ $a^{5}I^{\circ}_{6} - 25_{5}$ | (1.143) (1.064) | 1.073 1.209 1.080 |
| 4332.487 4331.472 4329 415 | 30 5 50 | | | 23074.97 23080.37 23091 34 | -6 +21 - 6 | $a^{3}I^{\circ}_{5} - 13_{6}$ $a^{5}L^{\circ}_{6} - z^{5}H_{5}$ $a^{3}I^{\circ}_{5} - z^{3}I_{6}$ | (0.860) | 1 000 | 3997.054 3994.834 2080 718 | 100 300 | | 6v 6v | 25011.38 25025.28 | -2 -28 -28 | $a^{5}I^{\circ}_{7} - z^{3}K_{7}$ $a^{5}I^{\circ}_{5} - z^{5}H_{4}$ | (1.177) 0.89 | 1.101 0.89 |
| 4327.698 4323.922 | 3 35 | - 6 | br | 23100.50 23120.67 | $-\frac{8}{-17}$ | $a^{5}K^{\circ}_{5} - 26_{5}$ $a^{3}I^{\circ}_{6} - 24_{6}$ | (0.000) | | 3982.063 3972.164 | $125 \\ 125 \\ 125$ | III é | 6r 6v | 25105.53 25168.11 | $-\frac{27}{3}$ - 1 | $a^{5}I^{\circ}_{6} - z^{5}H_{6}$ $a^{5}I^{\circ}_{5} - 17_{6}$ | (1.037) 0.877 | 1.106 1.118 |
| 4323.551 4314.74 4313.843 | 100 2 4 | IV 6 | ir | 23122.65 23169.87 23174.69 | + 9 + 20 - 4 | $a^{3}I^{\circ}_{7} - z^{5}I_{8}$ $a^{5}I^{\circ}_{6} - 13_{6}$ $a^{5}I^{\circ}_{5} - 8_{5}$ | (1.143) | 1.167 | 3971.164 3966.573 3965 263 | 100 100 100 | | 6r 6v 6v | 25174.44 25203.57 25211.00 | -16 + 1 + 1 = 8 | $a^{3}I^{\circ}_{6} - z^{3}I_{7}$ $a^{5}I^{\circ}_{7} - z^{5}I_{8}$ $a^{5}I^{\circ}_{4} - z^{5}I_{7}$ | (1.037) (1.177) (1.064) | $1.187 \\ 1.154 \\ 1.128$ |
| 4308.457 4305.763 | $20 \\ 150 \\ 60$ | III 6 | dva . | 23203.66 23218.18 | $+ \frac{1}{9}$ - 6 | $a^{3}I^{\circ}{}_{5} - 14_{5}$ $a^{5}I^{\circ}{}_{5} - z^{5}I_{4}$ | 0.877 | 0.683 | 3964.825 3964.261 | 125 60 | | 6v 6r | 25214.68 25218.27 | 0 | $a^{5}I^{\circ}_{5} - z^{5}I_{6}$ $a^{3}I^{\circ}_{5} - z^{3}H_{6}$ | (0.875) 0.858 | 1.039 |
| 4297.764 4292.351 | 50 50 4 | III 6 | Br | 23237.95 23261.40 23290.72 | $^{+25}_{+10}$ + 8 | $a^{5}I^{\circ}_{6} - 25_{5}$ $a^{5}I^{\circ}_{4} - 7_{5}$ $a^{5}K^{\circ}_{5} - 28_{5}$ | (1.037) 0.601 | 0.895 | 3962.445 3953.516 3949.438 | 60 150 150 | | 6?a 6v 6n | 25229.83 25286.81 25312.92 | -6 + 7 + 1 | $a^{3}I^{\circ}{}_{5} - z^{5}H_{5}$ $a^{5}I^{\circ}{}_{8} - z^{3}K_{8}$ $a^{5}I^{\circ}{}_{6} - z^{3}H_{6}$ | $0.869 \\ (1.250) \\ 1.08$ | $1.108 \\ 1.145 \\ 1.08$ |
| 4290.99 4288.830 4282.440 | 5 8 75 | TV 6 | | 23298.11 23309.85 | -10 - 19 | $a^{5}I^{\circ}_{6} - 14_{5}$ $a^{5}K^{\circ}_{7} - z^{3}K_{8}$ | 1.045 | | 3947.633 3935.823 | 125 125 | | 6v 6?va | 25324.49 25400.48 | -4 +21 | $a^5I^{\circ}_6 - z^5H_5$ $a^5I^{\circ}_5 - 18_5$ | (1.064) (0.875) | $1.125 \\ 0.990$ |
| 4272.271 4263.805 | 50 50 | III 6 IV 6 | dv dv dv | 23344.03 23400.18 23446.65 | + 4 -10 | $a^{5}I^{\circ}_{7} - 22_{6}$ $a^{5}I^{\circ}_{7} - 23_{7}$ | 1.245 | 0.991 | 3927.454 3925.456 3920.524 | 80 125 30d | III 6 III 3 III 2 | 6?ra 3a 2a | 25454.60 25467.56 25499.60 | $^{+10}_{+6}_{+10}$ | $a^{3}I^{\circ}_{5} - 26_{5}$ $a^{5}I^{\circ}_{4} - z^{5}H_{4}$ $a^{5}I^{\circ}_{4} - 16_{5}$ | $0.859 \\ 0.603 \\ (0.605)$ | $1.066 \\ 0.903 \\ 0.985$ |
| $4261.796 \\ 4259.64 \\ 4254 420$ | 15 5d 35 | | bra Br | 23457.71 23469.58 23408 38 | $^{0}_{+22}$ | $a^{3}I^{\circ}_{6} - z^{5}I_{7}$ $a^{5}L^{\circ}_{7} - z^{3}I_{7}$ $a^{3}I^{\circ}_{7} - z^{3}I_{7}$ | (1 142) | | 3918.856 3912.898 | 100 150 | III 4 III 4 | 4a 4a | 25510.45 25549.29 | +8 + 15 + 15 | $a^{5}I^{\circ}_{7} - z^{5}H_{6}$ $a^{5}I^{\circ}_{6} - 26_{5}$ | (1.177) (1.064) | 1.094 1.097 |
| 4249.484 4247.662 | 20 60 | V 6 III 6 | dia dia | 23525.67 23535.75 | $^{+2}_{-9}$ | $a^{5}I^{\circ}_{7} - 24_{6}$ $a^{5}I^{\circ}_{5} - 11_{6}$ | (1.143) (1.177) 0.878 | 0.98 1.156 | 3899.555 3889.330 | 100 10 150 | $\frac{1}{1V}$ 5 | 5a | 25636.71 25704.11 | $^{+10}_{-2}$ +13 | $a^{3}I^{\circ}_{5} - 2^{3}H_{7}$ $a^{3}I^{\circ}_{5} - 27_{6}$ $a^{5}I^{\circ}_{5} - 19_{5}$ | (0.875) | 1.025 |
| 4243.528 4241.019 4236.210 | 20 50 20 | III 6 IV 6 III 6 | ir v | 23558.69 23572.62 23599.38 | -11 0 -13 | $a^{3}I^{\circ}_{6} - z^{3}H_{6}$ $a^{5}I^{\circ}_{8} - z^{3}K_{7}$ $a^{5}I^{\circ}_{6} - 15\pi$ | 1.022 (1.250) (1.064) | (1.073) 1.108 | 3885.190 3884.741 | 100 | IV 4 | 1a | 25731.51 25734.48 25720 12 | +14 - 9 | $a^{5}I^{\circ}_{6} - 27_{6}$ $a^{5}I^{\circ}_{5} - 20_{6}$ | 1.058 | 1.068 |
| 4225.327 4222.98 | $50 \\ 125 \\$ | III 6 III 6 | ir iv | 23660.17 23673.31 | -10 - 16 | $a^{5}I^{\circ}_{4} - z^{5}I_{4}$ $a^{5}I^{\circ}_{5} - z^{5}K_{6}$ | 0.604 0.877 | 0.685 0.961 | 3878.307 3868.578 | 15 | _ | | 25777.17 25841.99 | $-11 \\ -22$ | $a^{5}I^{6}_{6} - 297$ $a^{5}I^{6}_{4} - 185$ | | _ |
| 4213.96 4208.305 4206.739 | 12 18 50 | III 6 III 6 | ora Sv | 23723.99 23755.87 23767.71 | $^{+14}$ + 2 - 7 | $a^{3}I^{\circ}{}_{5} - z^{5}H_{4}$ $a^{3}I^{\circ}{}_{5} - 16_{5}$ $a^{5}I^{\circ}{}_{8} - z^{5}I_{8}$ | (0.860) | 0.980 | 3868.125 3826.708 3823.571 | $\frac{4}{10}$ | _ | _ | 25845.02 26124.74 26146.17 | $^{+10}_{+3}$ | $a^{5}I^{\circ}_{5} - 21_{5}$ $a^{5}L^{\circ}_{6} - 2^{5}H_{7}$ $a^{5}I^{\circ}_{4} - 19_{5}$ | | |
| 4191.615 4189.518 | $\begin{array}{c} 40\\100\end{array}$ | III 6 III 6 | iv iv | 23850.45 23862.39 | -4 -13 | $a^{5}I^{\circ}_{6} - 16_{5}$ $a^{5}I^{\circ}_{7} - z^{5}I_{7}$ | (1.064) 1.175 | $0.985 \\ 1.121$ | $3803.110 \\ 3792.435$ | 50d 4 | | _ | 26286.83 26360.82 | -3 + 12 | $a^5I^{\circ}_4 - 21_5$ $a^5I^{\circ}_6 - z^3K_7$ | | |
| 4179.422 4172.273 | 200 75 | III 6 III 6 | v v | 23920.04 23961.02 | -13 - 5 - 3 | $a^{\circ}I^{\circ}_{5} - z^{\circ}I_{6}^{\circ}$ $a^{\circ}I^{\circ}_{6} - z^{\circ}K_{7}^{\circ}$ $a^{\circ}I^{\circ}_{6} - 17_{6}^{\circ}$ | 1.061 (1.064) | (1.062) 1.14 | 3769.695 3711.099 3710.012 | 20d 8d 6 | V 2 V - | 2a | 26519.84 26938.56 26946.45 | -14 + 12 + 18 | $a^{5}I^{\circ}_{5} - z^{3}H_{6}$ $a^{5}I^{\circ}_{5} - 27_{6}$ $a^{5}I^{\circ}_{5} - 28_{5}$ | | |
| 4171,824 4169,459 4168,08 | $75 \\ 15 \\ 20$ | III 6 V 6 | iv ir | 23963.60 23977.19 23985.12 | -1 -7 +3 | $a^{5}I^{\circ}_{7} - z^{3}H_{6}$ $a^{3}I^{\circ}_{6} - 27c$ $a^{3}I^{\circ}_{6} - 28c$ | (1.177) | 1.074 | 3699.952 3650.176 | $12 \\ 30$ | | | 27019.72 27388.16 | -6 - 5 | $a^{5}I^{\circ}_{7} - z^{5}H_{7}$ $a^{5}I^{\circ}_{4} - 28_{5}$ | 0.607 | 0.888 |
| | | | | | 1.0 | | | | | | | | | | | | |

The complexity introduced by h.f.s., coupled with the natural richness of the spectrum, has made the disentangling of overlapping patterns difficult, and less precision can be expected in the g values than is obtained with a spectrum consisting mostly of sharp lines.¹⁰ Where a g value is in parenthesis the pattern of the line was incomplete, overlapped, or unresolved, so this g value was assumed from the average for the level, and the other g value was calculated from

this and the experimental data. In other cases unresolved n patterns were used, a procedure which introduces small errors.

On account of the complexity of the patterns and the necessity of using exposures at various field strengths to interpret them, any table of actual measurements would be unduly extensive even if reported in abbreviated notation.¹⁰ For this reason only final g values are given, their use being to substantiate the quantum numbers assigned, and detailed results are held for a later report.

 $^{^{10}}$ G. R. Harrison, W. E. Albertson, and N. Hosford, J. Opt. Soc. Am. $31,\,439$ (1941).

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| $a^{5}K^{*}_{9}$ 8958.35 — 5 1.222 1.219 1 237 20443.00 — 6 — 1.00 $a^{5}L^{*}_{90}$ 9254.94 — 1 1.200 1.19 0 24 a 26523.96 — 4 — 1.02 $a^{3}H^{\circ}_{3}$? 9378.57 — 8 1.033 1.044 0 25 $_{5}$ 26640.82 — 6 — 1.075 $b^{5}I^{\circ}_{8}$ 9646.60 — 11 1.071 1.073 1 $z^{5}I_{7}$ 26860.83 — 10 1.179 1.123 $b^{4}I^{\circ}_{8}$ 26944.65 — 7 1.170 1.153 1 $z^{3}Hz$ 26961.92 — 9 1.167 1.073 | 3 |
| $a^{5}L^{-}_{10}$ 9294.94 — 1 1.200 1.19 0 246 2053.96 — 4 — 1.02 $a^{3}H^{\circ}_{2}$ 9378.57 — 8 1.033 1.044 0 255 26640.82 — 6 — 1.075 $b^{5}I^{\circ}_{6}$ 9646.60 — 11 1.071 1.073 1 $s^{5}I_{7}$ 26860.83 — 10 1.179 1.123 $b^{5}I^{\circ}_{2}$ 11005 45 — 7 1.170 1.153 | 1 |
| $a^{3}H^{5}x_{5}$ 93/8.57 — 8 1.035 1.044 0 255 20640.82 — 0 — 1.075 $b^{5}I^{9}_{6}$ 9646.60 — 11 1.071 1.073 1 $z^{5}I_{7}$ 26860.83 — 10 1.179 1.123 $b^{5}I^{9}_{6}$ 11005.45 — 7 1.170 1.153 1 $z^{3}H_{6}$ 26961.92 — 9 1.167 1.073 | 1 |
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| | 3 |
| $U_{11} = 11000.10$ $I = 1117 11100$ $I = 2011 2001724$ $I = 1100 1101$ | 4 |
| $b^{5}I^{6}_{8}$ 11610.92 — 6 1.250 1.231 2 $z^{2}H_{5}$ 20973.54 — 5 1.100 1.101 | 1 |
| 15 $216/6.28$ — 6 — 1.001 2 $2^{\circ}K_{8}$ $2/12/.88$ — 9 1.135 1.145 | 1 |
| 25 22039.98 — 1 — 0.997 4 205 27198.15 — 1 — 1.007 | å |
| 35 $225/1.38$ — 1 — 1.105 4 276 2730.36 — 0 — 1.00 | 1 |
| $2^{\circ}N_5$ 220/5.40 - 0 0.007 0.821 4 265 27366.21 - 6 - 0.000 | ò |
| 4_{6} 22/18.31 — 7 — 1.10 0 297 27423.29 — 0 — 1.075 | 4 |
| 5_5 22885.30 — 7 — 0.994 2 308 27/61.03 — 8 1.018 1106 | ž |
| 0_{6} 23141.37 — 5 — 1.002 1 2*K7 23009.71 — 6 1.015 1.000 | 1 |
| 7_5 23201.30 - 4 - 0.390 3 218 26201.37 6 1.200 11.07 | 1 |
| 85 23010.07 - 5 - 1.000 1 2715 2350.08 - 0 1.214 1.105 | 3 |
| 2^{214} 23000.18 - 5 0.000 0.064 2 2^{214} 28077.72 - 7 1.130 1.001 | ŏ |
| y_7 23093.23 - 0 - 1.107 2 $z^{27}Ky$ 20010.04 - 4 1.222 1.217 | ĭ |
| $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | ô |

TABLE III. Pr II terms.

That so many values of o-c are less than 10 (i.e., less than 0.1 cm⁻¹) is gratifying, as it is difficult to make exact wave-length measurements on lines with partially resolved h.f.s. 132 lines are found to agree with the wave number calculated from the combination principle to within ± 0.05 cm⁻¹, and 78 more to within ± 0.10 , leaving only 108 with deviations greater than 0.10 cm⁻¹.

In the first column of Table III are listed the term assignments, followed by the wave number of each and the hyperfine structure deduced from all lines considered as arising from the term, where i indicates wider separations at lower wave numbers, and n at higher. The fourth column gives the number of combinations with the term in the present array. The fifth column contains the theoretical g value of a term of the designation given, calculated from Landé's formula for LS coupling. The next column contains the measured g value of the term, averaged from measurements on the number of resolved patterns given, or on unresolved patterns reduced from several plates. The observed g values are in most cases believed to be correct to within ± 0.005 unit.

LOW CONFIGURATIONS OF Pr II

In accordance with the Bohr-Stoner theory the normal praseodymium atom (Z=59) can be expected to have three electrons outside a closed shell. Pr II, with two such electrons, would have a simpler spectrum than Pr I, but in both cases two 6s electrons are present which are very loosely bound; and it is necessary in Pr II to take four electrons into account when predicting terms. Among the odd configurations to be expected are fds^2 , fd^2s , f^3s and f^3d . Even configurations which should be important are f^2ds , f^2s^2 , f^3p , and f^4 .

Many of the strongest lines of Pr II, which presumably arise from low levels, show wide h.f.s. patterns. These usually arise when a single s electron occurs in a configuration, making

TABLE IV. Expected important terms of Pr II.

| 4f ³ 6s | ^{5, 3} (<i>IGFDS</i>)°, ^{3, 1} (<i>LKIH</i> ₂ <i>G</i> ₂ <i>F</i> ₂ <i>D</i> ₂ <i>P</i>)° |
|--------------------|---|
| $4f^{3}5d$ | ^{5,3} (LKIHG, IHGFD, HGFDP, GFDPS, D)° ^{3,1} ($NML_2K_4I_6H_7G_9F_9D_7P_5S_3$)° |
| 4f36p | $^{5,3}(KIH, HGF, GFD, FDP, P)$ $^{3,1}(ML_2K_3I_4H_5G_6F_6D_5P_3S)$ |

| | $a^5 I^{\circ}_8$ | $a^5 I^{\circ}_7$ | a ⁵ I° ₆ | $a^5 I^{\circ_5}$ | a ⁵ I°4 | $a^{3}I^{\circ}_{7}$ | $a^{3}I^{\circ}_{6}$ | $a^{3}I^{o}_{5}$ |
|---------------------------------------|-------------------------------------|---|--|---|-----------------------------------|--|---|--|
| z ⁵ K9 8 7 6 5 | 200 III 6v 100 IV 6v X X | X 200 III 6v 100 III 6v 100 V 6v X | $\begin{array}{c} X \\ X \\ 200 \text{ III } 6v \\ 125 \text{ III } 6v \\ 15 - 6v \end{array}$ | X X X 125 III 6v 200/ III 6v | X X X 125 III 6r | $ \begin{array}{c} $ | $\begin{array}{c} X \\ X \\ 200 \text{ III } 6r \\ 40 - 6r \\ - \end{array}$ | X X 125 III 6r |
| $z^{3}K_{8}$ 7 6 | 150 III 6v 50 IV 6v X | 100 III 6v 3 | 4 <u>-</u> | X X | X X X | 100 III 6r 100 IV 6r | X 150 III 6r 60 V 6r | X X 90 III 6ra |
| z ⁵ /8 7 6 5 4 | 50 III 6v 90 V 6v X X X | 100 III 6v 100 III 6v 50 IV 6v X X | X 100 III 6v 200 III 6v 150 IV 6v X | X X 125 III 6v 250 III 6v 150 III 6va | X X 50 III 6ra 50 III 6r | $\begin{array}{c} 100 \text{ IV } 6r \\ 5d & - \\ x \\ x \\ x \end{array}$ | $\begin{array}{c} X \\ 15 \text{ IV} \\ 25 \text{ V} \\ \overline{\text{ fr}} \\ \overline{\text{ fr}} \end{array}$ | $\begin{array}{c} X \\ X \\ 8 \\ \end{array}$ |
| z ³ I7 6 5 | 150 III 6v X X | 40 V 6v | _ | <u>x</u> | X X | $\begin{array}{c} 35 \text{ IV} & 6r \\ 2 & - \\ X \end{array}$ | 100 III 6r 100 V 6r | 50 IV 6?r?a |
| z ⁵ H7 6 5 4 3 | 100 IV 5?a X X X X X | $\begin{array}{ccc} 12 & - & - \\ 100 & III & 4a \\ & X \\ & X \\ & X \\ & X \end{array}$ | 125 IV 6v X X | X | X X 125 III 3a | 150 III 6r X X X | 125 III 6r X X | $ \begin{array}{c} $ |
| z ³ H6 5 | X X X | 75 III 6v X X | 150 III 6v X | 20d V 2a | х | $30 \frac{1}{X}$ | 20 III 6r X | 60 III 6r |

TABLE V. Principal supermultiplet of Pr II.*

* X—indicates line forbidden by selection principle for ΔJ . ——indicates line not found.

plausible the assumption that the lowest terms of Pr II arise from such a configuration. Three likely configurations are then fd^2s , f^2ds and f^3s . Resulting terms of the latter are given in Table IV. When Hund's theory and Meggers and Laporte's rule are used the lowest terms to be expected from these three configurations are ${}^{5}I^{\circ}_{4}$, ${}^{5}K_{5}$, and ${}^{5}I^{\circ}_{4}$, respectively.

Our analysis indicates that the level $f^{3}({}^{4}I^{\circ})$ $\cdot s^5 I^{\circ}_4$ is the lowest. As will be seen from Fig. 1, all eight levels of the low ${}^{5}I^{\circ}$ and ${}^{3}I^{\circ}$ terms arising from the addition of an *s* electron to the parent ⁴*I*° term of Pr III have been found. Combinations of these terms with the even triads 5KIH and ^{3}KIH which arise from the $f^{3}p$ configuration give rise to the strongest lines of the spectrum. The raies ultimes of praseodymium are usually given¹¹ as 4179.422 and 4062.817A. These lines we have classified as $a^5I^{\circ}_6 - z^5K_7$ and $a^3I^{\circ}_6 - z^3K_7$. From the usual multiplet intensity rules one would expect the leading line of the supermultiplet to be strongest, with a prediction of $a^5 I_8^\circ - z^5 K_9$ as the raie ultime. This line, at 4100.746, is of intensity 200, but other lines are stronger. The estimated intensities of the lines of the basic supermultiplet are given in Table V, where an irregularity in intensities is to be noted. A similar irregularity is found in the homologous supermultiplet of Nd II.¹² The intensities need more careful study before the cause of this anomaly can be explained.

Hyperfine Structure

The eight levels of the terms $f^{3}({}^{4}I^{\circ}) \cdot s^{5}I^{\circ}$ and ${}^{3}I^{\circ}$ have marked hyperfine structure which appears to be due mainly to the interaction of the 6s electron with the moment of the nucleus. It is of interest to apply to this case the equations given by Goudsmit and Bacher.¹³ The change in atomic energy due to the interactions between electronic and nuclear moments (h.f.s.) is given by

$$\Gamma_F = \frac{1}{2} A \left[F(F+1) - I(I+1) - J(J+1) \right], \quad (1)$$

where J represents the mechanical moment of the electrons, I that of the nucleus (= 5/2 for Pr), F the total moment, and A is a number independent of F.

If we assume that the hyperfine structure is due to the *s* electron and that there is JJ coupling between the latter and the ion, then, as shown by Goudsmit and Bacher,

$$A = a \frac{J(J+1) + s(s+1) - J'(J'+1)}{2J(J+1)}, \qquad (2)$$

¹² McNally, Harrison, and Albertson, to be published shortly.

¹¹ M. I. T. Wavelength Tables.

shortly. ¹³ S. Goudsmit and R. F. Bacher, Phys. Rev. **34**, 1501 (1929).



FIG. 2. Zeeman patterns of Pr II line showing hyperfine structure. Below, no-field pattern; middle, n components; above, p components. The strong line at the left is λ 4368.327A.

where s is the spin of the electron $(=\frac{1}{2})$, J' the moment of the ion, and a a constant which measures the strength of the interaction between the s electron and the nuclear moment.

There are two cases to be considered. For the levels ${}^{b}I^{o}_{5, 6, 7, 8}$

and (2) gives
$$J' = J - \frac{1}{2}$$

$$A = a/2J.$$
(3)

 $J' = J + \frac{1}{2}$

For the levels ${}^{5}I^{\circ}_{4}$ and ${}^{3}I^{\circ}_{5, 6, 7}$

and

$$A = -a/[2(J+1)].$$
 (4)

The difference in signs of (3) and (4) is in agree-

ment with the observed difference in the shading of the h.f.s. for lines involving the two groups of levels.

For J>1, the total width of the hyperfine structure $\Delta\sigma$ is found from (1) to be given by

$$\Delta \sigma = \Gamma_{J+I} - \Gamma_{J-I} = A I (2J+1). \tag{5}$$

In attempting to make a quantitative comparison of theory and observation, one is confronted with the difficulty that there is a great deal of variation in the measured h.f.s. data¹ for lines going to a common level that is responsible for the observable h.f.s. One can take an average over these lines to get information about the level in question, but it is to be expected that some uncertainty will remain.

Table VI gives the $\Delta\sigma$ values for the eight levels as determined from White's h.f.s. data for those lines the classification of which we have confirmed with Zeeman measurements. A minus sign indicates that the h.f.s. is inverted. From the $\Delta\sigma$ in each case the corresponding value of *a* was calculated by means of (5) and (3) or (4). The various calculated values differ somewhat,

TABLE VI. Values of $\Delta \sigma$ from White's h.f.s. data.

| Level | $\Delta \sigma$ (obs.) | a(CALC.) | $\Delta \sigma(\text{CALC}).$ |
|--------------------------------------|------------------------|----------|-------------------------------|
| 5 I°4 | -0.80 | +0.36 | -0.90 |
| 3I° 5 | -0.74 | 0.32 | -0.92 |
| 31°6 | -0.84 | 0.36 | -0.93 |
| 3I°7 | -0.91 | 0.39 | -0.94 |
| ⁵ <i>I</i> ° ₅ | +1.13 | 0.41 | +1.10 |
| ⁵ <i>I</i> ° ₆ | +1.10 | 0.41 | +1.08 |
| 5 I°7 | +1.05 | 0.39 | +1.07 |
| ⁵ <i>I</i> ° ⁸ | +1.11 | 0.42 | +1.06 |
| | | | |

TABLE VII. g sums for $f^{3}({}^{4}I^{\circ}) \cdot s$ levels of Pr II.

| Term | g(meas.) | g(LS) | $g(J_j)$ | J_{i} | SUM g(MEAS.) | SUM g(THEOR.) |
|--|----------------|----------------|------------------|--|--------------|---------------|
| a ⁵ I°4 | 0.605 | 0.600 | 0.600 | $(4\frac{1}{2}, \frac{1}{2})$ | | |
| | | | | | 0.605 | 0.600 |
| a ⁵ I°5 a ³ I°5 | 0.875 0.860 | 0.900 0.833 | 0.855 0.878 | $(4\frac{1}{2}, \frac{1}{2}) \\ (5\frac{1}{2}, \frac{1}{2})$ | | |
| | | | | | 1.735 | 1.733 |
| $a^{5}I^{0}_{6}_{6}$ $a^{3}I^{0}_{6}$ | 1.064 1.037 | 1.071 1.024 | $1.051 \\ 1.044$ | $(5rac{1}{2},rac{1}{2})\ (6rac{1}{2},rac{1}{2})$ | | |
| | | | | | 2.101 | 2.095 |
| a ⁵ I°7 a ³ I°7 | 1.177 1.143 | 1.179 1.143 | $1.171 \\ 1.151$ | $(6\frac{1}{2}, \frac{1}{2}) (7\frac{1}{2}, \frac{1}{2})$ | | |
| | | | | | 2.320 | 2.322 |
| a ⁵ I° 8 | 1.250 | 1.250 | 1.250 | $(7\frac{1}{2}, \frac{1}{2})$ | | |
| | | | | | 1.250 | 1.250 |

| | | 9 | | 8 | | 7 | | 6 | | 5 | | 4 |
|---------------------------|-------|-------|---------|--------|---------|---------|---------|----------|-------|--------|-------|--------|
| - | g M | gT | g M | gT | g M | gT | g M | g T | g M | g T | g M | g T |
| z^5K_5 | | | | | | | | | 0.821 | 0.667 | | |
| $z^{5}I_{4}$ | | | | | | | | - | | | 0.684 | 0.600 |
| $z^{5}K_{6}$ | | | | | | | 0.959 | 0.905 | | | | |
| $z^{3}K_{6}$ | | | | | | | 0.992 | 0.857 | | | | |
| Z ^b 15 | | | | | | | | | 0.911 | 0.900 | | |
| $z^{3}I_{6}$ | | | | | | | 1.009 | 1.024 | | | 0.007 | 0 000 |
| $z^{\mathfrak{d}}H_4$ | | | | | 1.060 | 4.054 | | | | | 0.905 | 0.900 |
| Z ⁹ K7 | | | | | 1.062 | 1.054 | 1 0 1 0 | 1 071 | | | | |
| 2º16 | | | | | 1 1 2 2 | 1 1 70 | 1.042 | 1.071 | | | | |
| Z ³ 17 ~311 | | | | | 1.123 | 1.179 | 1 072 | 1 167 | | | | |
| 2°116 ~511 | | | | | | | 1.075 | 1.107 | 1 101 | 1 100 | | |
| $2^{\circ}\Pi_{5}$ | | | 1 1 / 3 | 1 153 | | | | | 1.101 | 1.100 | | |
| 2°11.8 ~3 V | | | 1.145 | 1.155 | 1 106 | 1 018 | | | | | | |
| 2°IX 7 75 I. | | | 1 1 5 4 | 1 250 | 1.100 | 1.018 | | | | | | |
| 25H. | | | 1.154 | 1.230 | | | 1 103 | 1 214 | | | | |
| 231_ 231_ | | | | | 1 187 | 1 1 4 3 | 1.105 | 1.214 | | | | |
| $\frac{1}{7} K_{0}$ | 1 217 | 1 222 | | | 1.107 | 1.140 | | | | | | |
| z5H. | 1.417 | 1.444 | | | 1.215 | 1.286 | | | | | | |
| ~ 11 / | | | | | | 1.200 | | | | vii | | |
| Sums | 1.217 | 1.222 | 2.297 | 2.403* | 5.693 | 5.680 | 6.178 | 6.238 | 2.833 | 2.667* | 1.589 | 1.500* |

TABLE VIII. g sums for even levels of Pr II.

* Indicates that all terms of that particular j value derivable from parent term 4I + p have not been found and g sum rule is not applicable. This assumes that 4I is perfect LS coupling.

partly because of errors in the values of $\Delta \sigma$ and partly, probably, because of incomplete JJcoupling, etc. By taking

$a = 0.40 \text{ cm}^{-1}$,

the value of $\Delta \sigma$ was calculated in each case on the basis of the above equations. It is evident that the agreement is quite satisfactory.



FIG. 3. Effect of a strong magnetic field in breaking a normal hyperfine-multiple level, $a^5I^{\circ}_4$, containing six levels, up into 54 levels.

In the presence of the magnetic field which is used to produce the Zeeman effects, the character of the h.f.s. changes completely. The magnetic field used in practice is a strong field from the standpoint of the h.f.s. and hence it destroys the coupling between I and J, so that the component of each in the direction of the field is quantized nearly independently (Back-Goudsmit effect).¹⁴

In this case the change in atomic energy due to the external magnetic field and the magnetic moment of the nucleus is given by

$$\Delta E = (-g_I M_I + gM) \frac{He}{4\pi mc^2} + A M_I M, \quad (6)$$

where M and M_I are the components along the field of J and I, respectively, A is the same constant as in (1), g is the usual g factor for the extra-nuclear electrons, and g_I is the nuclear g factor. Since g_I is usually small compared to g, one can take

$$\Delta E = gM \frac{He}{4\pi mc^2} + AM_IM. \tag{7}$$

The first term in the right-hand member corresponds to the ordinary Zeeman effect, the

¹⁴ E. Back and S. Goudsmit, Zeits. f. Physik **47**, 174 (1928).

second gives the h.f.s. In this case, the width of the h.f.s. is given by

$$\Delta \sigma = (\Delta E) M_I = +I - (\Delta E) M_I = -I. \tag{8}$$

Hence in a Zeeman pattern, the sharpest lines should be found near the center of the p and of each *s* branch, for which cases |M| is a minimum. An example of this is to be seen in Fig. 2, which shows the no-field line 4368.327A and its Zeeman pattern. A diagram of the h.f.s. for the lower parent level of this line, $a^5I^{\circ}_4$ without and with a magnetic field, according to Eqs. (1) and (7), is given in Fig. 3, where the h.f.s. spacing has been exaggerated in comparison with the separations of the Zeeman components.

CALCULATION OF g SUMS

In Table VII are given the g sums for Pr II levels arising from the configuration $f^{3}({}^{4}I^{\circ}) \cdot s$. It will be noted that the agreement between the measured and theoretical sums is usually within a few tenths of a percent, though perturbations much greater than this cause deviations of the individual terms. In Table VIII, which gives the g sums for even levels, the agreement is not quite so satisfactory.

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On the ${}^{2}\Pi_{u} \rightarrow {}^{2}\Pi_{g}$ Bands of CO₂⁺. Part I

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The band spectrum appearing in emission in the region λ 2900-4300 and believed to belong to the CO₂⁺ or possibly CO2 molecule has been studied and the excitation conditions found to be in substantial agreement with the former results of Duffendack and collaborators and of Smyth. The bands have been obtained with great intensity and photographs of most of them have been made in the second order of the 30-foot grating (actually obtained resolving power of 350,000). The rotational structure and the excitation conditions show that most of the bands belong to an extensive $^2II{\longrightarrow}^2II$ system of bands of the molecule CO_2^+ . The molecule is linear in both states; the lower ² Π appears to be the ground state ² Π_g and the upper ²II is the first excited state ${}^{2}\Pi_{u}$ of this molecule predicted by Mulliken. The complete rotational and vibrational analysis of this band system is still in progress; in this

INTRODUCTION

W HEN a gas through which a discharge is passing contains carbon dioxide (or CO), in addition to the bands belonging to CO and CO⁺ a great number of bands appear in the spectrum in the region $\lambda 2800-4500$: the most

paper the analysis of 5 double bands of the $v''_1 = v''_2$ $=v''_3=0$ progression of the symmetrical vibration (v'_1) varying, $v'_2 = v'_3 = 0$ is presented. The results of the analysis are: $\nu_0^{(0,0)} = 28,532.60(^{2}\Pi_{3/2} \rightarrow ^{2}\Pi_{3/2})$ and $\nu_0^{(0,0)}$ =28,468.48(${}^{2}\Pi_{\frac{1}{2}} \rightarrow {}^{2}\Pi_{\frac{1}{2}}$). The vibrational intervals (i.e., the distances between the origins of successive bands in the progression) are: $\Delta G'_1 = 1126.71$; $\Delta G'_2 = 1122.66$; $\Delta G'_3$ =1120.22; $\Delta G'_4$ =1120.04 (all ${}^{2}\Pi_{3/2u}$) and $\Delta G'_1$ =1125.97; $\Delta G'_2 = 1120.79; \ \Delta G'_3 = 1116.09; \ \Delta G'_4 = 1111.76 \ (all \ ^2\Pi_{\frac{1}{2}u}).$ Further for ${}^{2}\Pi_{3/2g}B^{\prime\prime}{}_{0} = 0.3796$; for ${}^{2}\Pi_{\frac{1}{2}g}B^{\prime\prime}{}_{0} = 0.3812$; for ${}^{2}\Pi_{3/2u}B'_{0} = 0.3485; B'_{1} = 0.3475; B'_{2} = 0.3465; B'_{3}$ =0.3457; B'_4 =0.3453; for ${}^{2}\Pi_{\frac{1}{2}u}B'_0$ =0.3501; B'_1 =0.3492; $B'_2 = 0.3483$; $B'_3 = 0.3475$; $B'_4 = 0.3466$. The A-doubling is observable only in the ${}^{2}\Pi_{\frac{1}{2}} \rightarrow {}^{2}\Pi_{\frac{1}{2}}$ sub-bands in this progression; in ${}^{2}\Pi_{u}$ it is bigger than in ${}^{2}\Pi_{g}$ ($p''_{0}=0.004$ for $v''_1=0$) and increases fast with the vibrational energy.

prominent of these is the double band at $\lambda 2883$ –2896, which appears whenever the smallest traces of CO₂ (or CO) are present. All these bands have been observed by many investigators (some of them as far back as 1802), but there was considerable uncertainty about their emitter,



FIG. 2. Zeeman patterns of Pr II line showing hyperfine structure. Below, no-field pattern; middle, n components; above, p components. The strong line at the left is $\lambda 4368.327$ A.