# SERIES SPECTRA OF IONIZED PHOSPHORUS, $P_{II}$

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Abstract

One hundred and ten of the strong lines of $P_{II}$ have been classified as arising from various combinations between thirty-two terms of the triplet system. The observed terms are exactly those demanded by the Hund theory.

IN previous papers[1] by Professor Millikan and the author the series spectra of one, two, and three-valence-electron atoms of phosphorus ($P_{III}$, $P_{IV}$, and $P_V$) have been analyzed. The present paper is an extension of the same methods, combined with the predictions of the Hund theory, to the analysis of the spectra arising from the four-electron atom of phosphorus, ($P_{II}$).

According to the Hund theory the various configurations of a four-electron system such as $P_{II}$ should give rise to terms as shown in Table I.

TABLE I

*Spectroscopic terms in a four-electron system, according to the Hund theory.*

| Configuration | Designation | Types of Terms |
|---|---|---|
| $s^2p^2$ | $a$ | $^3P, {}^1S, {}^1D$ |
| $sp^3$ | $b$ | $^5S, {}^3S, {}^3P, {}^3D, {}^1P, {}^1D$ |
| $s^2p \cdot s$ | $k$ | $^3P, {}^1P$ |
| $s^2p \cdot p$ | $m$ | $^3S, {}^3P, {}^3D, {}^1S, {}^1P, {}^1D$ |
| $s^2p \cdot d$ | $n$ | $^3P, {}^3D, {}^3F, {}^1P, {}^1D, {}^1F$ |

In Table II which gives the results of this analysis of $P_{II}$ the terms arising from any configuration are designated by the letter appearing opposite it in the second column of Table I. In the case of terms due to the last three configurations of Table I the total quantum number of the excited electron is indicated in the usual way by a numeral preceding the designation of the term. Of course for $P_{II}$ all electrons in the $a$ and $b$ configurations and all electrons except the excited one in the $k$, $m$, and $n$ configurations are in three-total-quantum-number orbits.

While five terms arising from the $s^2p \cdot 4d$ configuration have been located, it has been impossible to determine the inner quantum numbers of these terms and consequently to sort them into components of the $^3P$, $^3D$, $^3F$ terms that are demanded by the Hund theory for this configuration. This is because certain of the possible lines, the knowledge of whose presence or absence is necessary for the determination of the inner quantum number, so nearly coincide with other strong lines that they could not be detected, even if present. For this reason all of these terms have been indicated by an X.

[1] Bowen and Millikan, Phys. Rev. **25**, p. 295, p. 591, p. 600 (1925).

## TABLE II

*Triplet series lines of $P_{II}$*

| Int. | λI.A.Vac. | ν | Designation | Int. | λI.A.Vac. | ν | Designation | Term Values | |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 782.550 | 127787.4 | $aP_1$–$4nX_4$ | 5 | 3473.86 | 28786.4 | $3nP_2$–$4mP_2$ | $aP_0$ | 160497.7 |
| 0 | 782.642 | 127772.3 | $aP_1$–$4nX_3$ | 3 | 3479.73 | 28737.9 | $3nP_1$–$4mP_2$ | $aP_1$ | 160332.4 |
| 1 | 782.960 | 127720.4 | $aP_1$–$4nX_2$ | 5 | 3503.99 | 28538.9 | $3nP_2$–$4mP_1$ | $aP_2$ | 160027.8 |
| 2 | 783.739 | 127593.5 | $aP_0$–$4nX_1$ | 4 | 3519.60 | 28412.3 | $3nP_1$–$4mP_0$ | | |
| 0 | 784.464 | 127475.6 | $aP_2$–$4nX_{2,4}$ | 4 | 3716.90 | 26904.1 | $3nP_2$–$4mD_3$ | | |
| 1 | 784.808 | 127419.7 | $aP_2$–$4nX_3$ | 3 | 3762.87 | 26575.5 | $3nP_2$–$4mD_2$ | | |
| 1 | 786.146 | 127202.8 | $aP_1$–$4nX_0$ | 4 | 3769.76 | 26526.9 | $3nP_1$–$4mD_2$ | $bP_1$ | 50243.8 |
| | | | | 2 | 3787.76 | 26400.8 | $3nP_2$–$4mD_1$ | $bP_2$ | 50205.2 |
| 0 | 810.28 | 123414.1 | $aP_2$–$5kP_2$ | 4 | 3794.67 | 26352.8 | $3nP_1$–$4mD_1$ | | |
| | | | | 3 | 3796.16 | 26342.4 | $3nP_0$–$4mD_1$ | | |
| 1 | 906.996 | 110254.1 | $aP_0$–$bP_1$ | | | | | | |
| 2 | 908.046 | 110126.6 | $aP_1$–$bP_2$ | 3 | 4034.81 | 24784.3 | $4mD_1$–$4nX_4$ | $bD_1$ | 56443.1 |
| 2 | 908.356 | 110089.0 | $aP_1$–$bP_1$ | 3 | 4037.35 | 24768.7 | $4mD_1$–$4nX_3$ | $bD_2$ | 56394.7 |
| 2 | 910.554 | 109823.3 | $aP_2$–$bP_2$ | 4 | 4063.22 | 24611.0 | $4mD_2$–$4nX_4$ | $bD_3$ | 56301.3 |
| 2 | 910.884 | 109783.5 | $aP_2$–$bP_1$ | 4 | 4065.78 | 24595.5 | $4mD_2$–$4nX_3$ | | |
| | | | | 5 | 4073.27 | 24550.3 | $4mD_3$–$4nX_2$ | | |
| 2 | 961.024 | 104055.7 | $aP_0$–$bD_1$ | 5 | 4092.68 | 24433.9 | $4mD_1$–$4nX_1$ | | |
| 3 | 962.124 | 103936.7 | $aP_1$–$bD_2$ | 4 | 4118.24 | 24282.2 | $4mD_2$–$4nX_4$ | $4kP_0$ | 73900.0 |
| 3 | 962.568 | 103888.8 | $aP_1$–$bD_1$ | 2 | 4121.93 | 24260.5 | $4mD_2$–$4nX_1$ | $4kP_1$ | 73753.6 |
| 2 | 964.074 | 103726.5 | $aP_2$–$bD_3$ | 6 | 4128.65 | 24221.0 | $4mD_3$–$4nX_2$ | $4kP_2$ | 73372.9 |
| 3 | 964.932 | 103634.2 | $aP_2$–$bD_2$ | 4 | 4131.93 | 24201.8 | $4mD_1$–$4nX_0$ | | |
| 3 | 965.400 | 103584.0 | $aP_2$–$bD_1$ | | | | | | |
| | | | | 1 | 4403.19 | 22710.8 | $4mP_0$–$4nX_3$ | | |
| 4 | 1149.970 | 86958.8 | $aP_1$–$4kP_2$ | 6 | 4415.52 | 22647.4 | $4mP_1$–$4nX_4$ | $5kP_0$ | 37153.3 |
| 4 | 1152.825 | 86743.4 | $aP_0$–$4kP_1$ | 5 | 4418.54 | 22631.9 | $4mP_1$–$4nX_3$ | $5kP_1$ | 37042.0 |
| 5 | 1153.995 | 86655.5 | $aP_2$–$4kP_2$ | 4 | 4427.18 | 22587.7 | $4mP_1$–$4nX_2$ | $5kP_2$ | 36606.5 |
| 4 | 1155.020 | 86578.6 | $aP_1$–$4kP_1$ | 6 | 4464.19 | 22400.5 | $4mP_2$–$4nX_4$ | | |
| 4 | 1156.985 | 86431.5 | $aP_1$–$4kP_0$ | 4 | 4467.35 | 22384.6 | $4mP_2$–$4nX_3$ | | |
| 4 | 1159.105 | 86273.5 | $aP_2$–$4kP_1$ | 6 | 4469.22 | 22375.3 | $4mP_0$–$4nX_1$ | | |
| | | | | 8 | 4476.51 | 22338.8 | $4mP_2$–$4nX_2$ | | |
| 3 | 1301.865 | 76812.9 | $aP_0$–$3nP_1$ | 4 | 4484.91 | 22297.0 | $4mP_1$–$4nX_1$ | $4mS$ | 54496.2 |
| 3 | 1304.485 | 76658.6 | $aP_1$–$3nP_0$ | 7 | 4532.04 | 22065.1 | $4mP_1$–$4nX_0$ | | |
| 2 | 1304.655 | 76648.6 | $aP_1$–$3nP_1$ | 2 | 4535.07 | 22050.4 | $4mP_2$–$4nX_1$ | | |
| 2 | 1305.505 | 76598.7 | $aP_1$–$3nP_2$ | 7 | 4556.08 | 21948.7 | $4mS$–$4nX_4$ | $4mP_0$ | 55273.2 |
| 3 | 1309.890 | 76342.3 | $aP_2$–$3nP_1$ | 7 | 4559.31 | 21933.1 | $4mS$–$4nX_3$ | $4mP_1$ | 55195.1 |
| 4 | 1310.720 | 76293.9 | $aP_2$–$3nP_2$ | 5 | 4629.99 | 21598.3 | $4mS$–$4nX_1$ | $4mP_2$ | 54947.8 |
| | | | | 6 | 4680.25 | 21366.4 | $4mS$–$4nX_0$ | | |
| 3 | 1532.49 | 65253.3 | $aP_0$–$3nD_1$ | | | | | | |
| 3 | 1535.86 | 65110.1 | $aP_1$–$3nD_2$ | 0 | 4825.18 | 20724.6 | $4mD_1$–$5kP_2$ | | |
| 2 | 1536.38 | 65088.1 | $aP_1$–$3nD_1$ | 4 | 4865.73 | 20551.9 | $4mD_2$–$5kP_2$ | $4mD_1$ | 57332.0 |
| 3 | 1542.29 | 64838.6 | $aP_2$–$3nD_3$ | 4 | 4928.53 | 20290.0 | $4mD_1$–$5kP_1$ | $4mD_2$ | 57158.5 |
| 2 | 1543.08 | 64805.5 | $aP_2$–$3nD_2$ | 7 | 4944.79 | 20223.3 | $4mD_3$–$5kP_2$ | $4mD_3$ | 56829.8 |
| | | | | 5 | 4955.70 | 20178.8 | $4mD_1$–$5kP_0$ | | |
| 1 | 2455.21 | 40729.7 | $3nD_2$–$4mS$ | 7 | 4971.02 | 20116.6 | $4mD_2$–$5kP_1$ | | |
| | | | | 4 | 5153.63 | 19403.8 | $4kP_0$–$4mS$ | | |
| 3 | 2482.71 | 40278.6 | $3nD_2$–$4mP_2$ | 6 | 5192.84 | 19257.3 | $4kP_1$–$4mS$ | $3nP_0$ | 83674.7 |
| 5 | 2484.90 | 40243.1 | $3nD_3$–$4mP_2$ | 9 | 5297.55 | 18876.7 | $4kP_2$–$4mS$ | $3nP_1$ | 83685.5 |
| 3 | 2496.70 | 40052.9 | $3nD_1$–$4mP_1$ | | | | | $3nP_2$ | 83733.9 |
| 4 | 2498.08 | 40030.7 | $3nD_2$–$4mP_1$ | 8 | 5317.54 | 18805.7 | $4kP_1$–$4mP_2$ | | |
| 4 | 2501.68 | 39973.1 | $3nD_1$–$4mP_0$ | 9 | 5346.20 | 18704.9 | $4kP_0$–$4mP_1$ | | |
| | | | | 8 | 5388.36 | 18558.5 | $4kP_1$–$4mP_1$ | | |
| 2 | 2604.49 | 38395.2 | $3nD_2$–$4mD_3$ | 7 | 5411.15 | 18480.4 | $4kP_1$–$4mP_0$ | $3nD_1$ | 95246.0 |
| 3 | 2606.79 | 38361.4 | $3nD_3$–$4mD_3$ | 10 | 5427.42 | 18425.0 | $4kP_2$–$4mP_2$ | $3nD_2$ | 95225.7 |
| 3 | 2625.54 | 38087.4 | $3nD_1$–$4mD_2$ | 7 | 5501.23 | 18177.8 | $4kP_2$–$4mP_1$ | $3nD_3$ | 95191.0 |
| 4 | 2626.94 | 38067.1 | $3nD_2$–$4mD_2$ | 4 | 5379.60 | 18588.7 | $4mP_1$–$5kP_2$ | | |
| 2 | 2629.33 | 38032.5 | $3nD_3$–$4mD_2$ | 8 | 5452.16 | 18341.4 | $4mP_2$–$5kP_2$ | | |
| 3 | 2637.56 | 37913.8 | $3nD_1$–$4mD_1$ | 5 | 5485.06 | 18231.3 | $4mP_0$–$5kP_1$ | | |
| 2 | 2638.97 | 37893.6 | $3nD_2$–$4mD_1$ | 6 | 5508.66 | 18153.2 | $4mP_1$–$5kP_1$ | $4nX_0$ | 33130.0 |
| | | | | 6 | 5542.72 | 18041.7 | $4mP_1$–$5kP_0$ | $4nX_1$ | 32897.9 |
| 6 | 3420.21 | 29238.0 | $3nP_2$–$4mS$ | 6 | 5584.88 | 17905.5 | $4mP_2$–$5kP_1$ | $4nX_2$ | 32608.4 |
| 6 | 3425.84 | 29189.9 | $3nP_1$–$4mS$ | | | | | $4nX_3$ | 32563.0 |
| 4 | 3427.16 | 29178.7 | $3nP_0$–$4mS$ | 6 | 5589.80 | 17889.7 | $4mS$–$5kP_2$ | $4nX_4$ | 32547.6 |
| | | | | 2 | 5729.27 | 17454.2 | $4mS$–$5kP_1$ | | |

As in $N_{II}$[2] the lines arising from the jump from the $sp^3$ configuration to the $s^2p^2$ configuration are present but they are relatively much weaker than in that element, apparently because the term values of the $sp^3$ configuration lie much closer to the ionization energy of the atom in $P_{II}$ than in $N_{II}$. The spectrum is also similar to that found by Fowler[3] for $Si_I$. Just as in $Si_I$ the $3nP$ term is inverted while all others are normal. In this respect the elements of the second row of the periodic table differ from the corresponding elements of the first row. For the lighter elements the $3nD$ term is normal while the $bD$ and the $bP$ terms are inverted.

From the table it is evident that all triplet lines which should be expected to appear strongly have been located. This is still another confirmation of the Hund theory and its great utility in the prediction of spectra.

In the table all wave-lengths above 2400A are taken from Geuter[4] and corrected to I.A. Vac. The term values are determined by making the $4kP_0$ and the $5kP_0$ terms follow a Rydberg formula.

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[2] Bowen, Phys. Rev. **29**, 231 (1927).
[3] Fowler, Phil. Trans. **225**, p. 1 (1925).
[4] Kayser, Handbuch der Spektroskopie, Vol. VI, p. 246.