

ENERGY LEVELS OF PXII

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The spectrum of phosphorus arising from its various stages of ionization has been observed and analysed by H. A. Robinson. His work is still unpublished for ionization stages higher than the fifth, but the results of his analysis from unpublished data are quoted by Charlotte E. Moore (1949). In course of a theoretical study of the atoms of the CI isoelectronic sequences, Naqvi (1953) found that Robinson's energy values of the level intervals of the configuration of PX are not in accordance with the trend of the isoelectronic sequence; they are in fact much lower. The present paper is a report on the energy levels belonging to PXII.

PXII belongs to the BeI isoelectronic sequence. The ground configuration for this sequence is $1s^2 2s^2$, and the electronic shells are completely filled giving rise to a single energy level, namely 1S_0 . The next excited configuration, $1s^2 2s 2p$ has four energy levels 1P_1 and $^3P_{2, 1, 0}$. We shall be chiefly concerned with the level intervals $^3P_2 - ^3P_1$ and $^3P_1 - ^3P_0$ of this configuration. Robinson's values for these intervals are

$$^3P_2 - ^3P_1 = 6600.0 \text{ cm.}^{-1}$$

$$^3P_1 - ^3P_0 = 3200.0 \text{ cm.}^{-1}$$

Naqvi (1951) made a theoretical study of this isoelectronic sequence in which he calculated the values of the mutual magnetic interaction integral M_0 and another parameter ζ' for the atoms of this sequence. The parameter ζ' which differs inappreciably from the spin-orbit interaction integral ζ , is given by

$$\zeta' = \zeta - 30 M_0 - 4 N^{-1} + 2N^1 \quad \dots \dots \dots (1)$$

where M_0 , N^{-1} , N^1 are mutual magnetic interaction integrals (for their definitions and that of ζ reference may be made to Condon and Shortley, 1935 and Marvin, 1947). Briefly the method is as follows:

The theoretical expressions for the energy of the levels, obtained by taking into account the complete spin-orbit interaction as well as the mutual magnetic interactions, are equated to the energy values obtained from spectroscopic analysis. These equations are

$$\left. \begin{aligned} ^3P_2 - ^3P_1 &= \zeta' + 12M_0 + \frac{\frac{1}{2}\zeta^2}{^1P_1 - ^3P_1} \\ ^3P_1 - ^3P_0 &= \frac{1}{2}\zeta' - 30M_0 - \frac{\frac{1}{2}\zeta^2}{^1P_1 - ^3P_1} \end{aligned} \right\} \dots \dots \dots (2)$$

They are then solved for the unknown parameters, ζ' and M_0 occurring in these equations.

Table I gives the values of ζ' and M_0 for the BeI isoelectronic sequence. It is clear that the value of M_0 for PXII is erroneous. Further if we plot the fourth roots of ζ' against the atomic numbers, the points lie fairly closely on a straight line, except the point for PXII which is below the line, indicating that the value of ζ' for PXII is lower than the trend along this sequence.

TABLE I

Sequence	ζ'	M_0
BeI ..	2.2	0.0137
BII ..	15.8	0.0555
CIII ..	55.0	0.1486
NIV ..	141.1	0.2416
OV ..	300.4	0.4639
FVI ..	566.0	0.7083
NeVII
NaVIII ..	1575	1.5833
MgIX ..	2436	1.1388
AlX ..	3591	2.0833
SiXI ..	5140	2.2361
PXII ..	6505	-2.388

As for the case of PX, we conclude that the discrepancy is on account of erroneous energy values for the levels of PXII. The extrapolated values of ζ' and M_0 are

$$\zeta' = 7130 \text{ cm.}^{-1}$$

$$M_0 = 2.45 \text{ cm.}^{-1}$$

Using these extrapolated values of ζ' and M_0 and equations (2) we obtain for the level intervals of PXII

$${}^3P_2 - {}^3P_1 = 7310 \text{ cm.}^{-1}$$

$${}^3P_1 - {}^3P_0 = 3340 \text{ cm.}^{-1}$$

These values are substantially different from those of Robinson quoted above.

In the 1953 paper, it was reported for a number of isoelectronic sequences that the level intervals belonging to a particular configuration fit remarkably well with a fourth degree polynomial. This conclusion has been further checked and extended. For the case of Cl isoelectronic sequence it was found that the fit was very poor if PX was included, whereas it became almost perfect when PX was excluded. We have found the same result to hold for the BeI isoelectronic sequence. When PXII is included, the fit with a fourth degree polynomial comes out to be extremely poor as is shown in Table II. However, when PXII is excluded, the fit is

TABLE II

Sequence	$[{}^3P_2 - {}^3P_1]_{\text{obs.}}$	$[{}^3P_2 - {}^3P_1]_{\text{calc.}}$	Δ (obs. - calc.)	$[{}^3P_1 - {}^3P_0]_{\text{obs.}}$	$[{}^3P_1 - {}^3P_0]_{\text{calc.}}$	Δ (obs. - calc.)
BeI ..	2.35	-31.96	34.31	0.68	-7.38	8.06
BII ..	16.40	64.19	-47.79	6.40	17.78	-11.38
CIII ..	56.80	91.84	-35.04	23.00	31.73	-8.73
NIV ..	144.20	133.59	10.61	63.20	59.58	3.62
OV ..	306.20	259.18	47.02	136.70	124.70	12.00
FVI ..	576.00	525.65	50.35	260.00	248.69	11.31
NeVII
NaVIII ..	1604.00	1645.88	-41.88	730.00	750.82	-20.82
MgIX ..	2472.00	2550.14	-78.14	1162.00	1163.32	-1.32
AlX ..	3660.00	3696.32	-36.32	1690.00	1703.41	-13.41
SiXI ..	5250.00	5077.88	172.12	2420.00	2383.84	36.16
PXII ..	6600.00	6675.58	-75.58	3200.00	3215.62	-15.62

considerably improved as can be seen from Table III. The extrapolated values for the level intervals are

$${}^3P_2 - {}^3P_1 = 7316 \text{ cm.}^{-1}$$

$${}^3P_1 - {}^3P_0 = 3348 \text{ cm.}^{-1}$$

TABLE III

Sequence	$[{}^3P_2 - {}^3P_1]$ calc.	Δ (obs. - calc.)	$[{}^3P_1 - {}^3P_0]$ calc.	Δ (obs. - calc.)
BeI ..	3.23	-0.88	-0.10	0.78
BII ..	14.62	1.78	7.57	-1.17
CIII ..	56.44	0.36	24.43	-1.43
NIV ..	145.61	-1.41	62.06	1.14
OV ..	307.33	-1.13	134.64	2.06
FVI ..	575.00	1.00	258.86	1.14
NeVII
NaVIII ..	1603.07	0.93	741.96	-11.96
MgIX ..	2471.52	0.48	1147.06	14.94
AlX ..	3661.99	-1.99	1696.30	-6.30
SiXI ..	5249.12	0.88	2419.20	0.80

The extrapolated values of the level intervals obtained by these two methods give results in fairly good agreement with one another. The following mean values should be adopted for the energy intervals, rounded off in the last significant figure

$${}^3P_2 - {}^3P_1 = 7310 \text{ cm.}^{-1}$$

$${}^3P_1 - {}^3P_0 = 3350 \text{ cm.}^{-1}$$

The energy values of the 1P_1 level of the $2s2p$ configuration of PXII as given by Robinson appears to be allright.

SUMMARY

H. A. Robinson's values for the energies of the three $3P$ levels of the configuration $1s^2 2s2p$ of PXII appear to be in error. They have therefore been calculated by two different methods of extrapolation along the isoelectronic sequence, which give results in good agreement with one another.

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