On $s^2p^4\ ^1S$ and $sp^5\ ^1P$ in the S I Isoelectronic Sequence

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A STRONG unidentified line in the extreme ultraviolet has been recognized for some time as strictly following the "irregular doublet" law through the five elements from chlorine to scandium. For various reasons it was suspected to be $s^2p^4\ ^1D-sp^5\ ^1P$, and this explanation has recently been confirmed through the identifications in Cl II by Kiess and de Bruin.[1] The data for the transition including those of Kiess and de Bruin for Cl II are collected in Table I, where the last column gives the value for $sp^5\ ^1P$ relative to the ground level $s^2p^4\ ^3P_2$. The observations for K IV, Ca V, and Sc VI are taken from Ekefors[2] and Beckman.[3] The A III line is contained in Boyce's paper on argon[4] with the classification $s^2p^4\ ^1S-sp^5\ ^1P$. In consequence of the new identification the previous values for both terms involved are shown to be in error. The term ^1S of the ground configuration s^2p^4 has been fixed for the higher members in the S I sequence[5] but—in spite of many efforts—a considerable uncertainty has remained about its position in S I, Cl II, A III, and K IV. It was expected that the newly-found term $sp^5\ ^1P$ would aid effectively in the search for ^1S, but unfortunately the combination $s^2p^4\ ^1S-sp^5\ ^1P$ seems to be quite faint, judging from the absence of the corresponding line in the tables for Sc and Ca. Nevertheless, it has been possible to find the arrangement discussed below, which probably solves the problem of locating $s^2p^4\ ^1S$ in the first four spectra of the S I sequence.

TABLE I. $3s^23p^4\ ^1D_2-3s3p^5\ ^1P_1$.

	Int.	λ	ν	Diff.	$3s3p^5\ ^1P_1$
Cl II	10	961.49	104005		115657
				26008	
A III	12	769.152	130013		144023
				24741	
K IV	15	646.188	154754		171140
				24264	
Ca V	10	558.602	179018		197849
				24059	
Sc VI	6	492.423	203077		224474

The level values of the ground configuration must show a quite smooth change in their relative position through the sequence. Specially suitable for the comparison in the actual case are the quantities $^1D-{}^3P_c$, $^1S-{}^1D$ and the Slater ratio $(^1S-{}^1D):(^1D-{}^3P_c)$, which are collected in Table II, including the new values suggested in the present note. As usual, ^3P_c denotes the mean of the ^3P levels, weighted according to $2J+1$. The last column gives the value for ^1S with reference to the ground-level $^3P_2$. For all the spectra tabulated[6,1,4,5] the term ^1D has been found and connected with the triplets. The trend of the ^1S position through the series Ti VII, Sc VI, and Ca V is definitely in favor of changing Ruedy's classification[6] in S I in the way suggested by Bowen,[7] to which the figures in the first row of Table II correspond. On this basis the difference $^1S-{}^1D$ can be accurately interpolated for A III. At the corresponding wave-length one finds the strongest unidentified nebular line as observed by Bowen and Wyse[8] in the three nebulae: *NGC* 6572 λ5190.8 (2), *NGC* 7027 λ5192.0 (5), and *NGC* 7662 λ5192? (3). If we accept the identification [A III] $^1S-{}^1D$ for this

TABLE II. Configuration $3s^23p^4$.

	$^1D-{}^3P_c$		$^1S-{}^1D$		$\frac{^1S-{}^1D}{^1D-{}^3P_c}$	^1S
S I	9044		12942		1.4310	22182
		2265		3308		
Cl II	11309		[16250]		[1.437]	[27900]
		2156		3007		
A III	13465		19257		1.4302	33267
		2105		2905		
K IV	15570		22162		1.4234	38548
		2096		2854		
Ca V	17666		25016		1.4161	43847
		2119		2825		
Sc VI	19785		27841		1.4072	49238
		2162		2803		
Ti VII	21947		30644		1.3963	54757

[1] C. C. Kiess and T. L. de Bruin, J. Research Nat. Bur. Stand. **23**, 443 (1939).
[2] E. Ekefors, Zeits. f. Physik **71**, 53 (1931).
[3] A. Beckman, Thesis, Upsala, 1937.
[4] J. C. Boyce, Phys. Rev. **48**, 400 (1935); ibid. **49**, 351 (1936).
[5] I. S. Bowen, Phys. Rev. **46**, 791 (1934), (Ca V); P. G. Kruger and H. S. Pattin, Phys. Rev. **52**, 621 (1937), (Sc VI); and B. Edlén, Zeits. f. Physik **104**, 188 (1937), (Ti VII, V VIII, Cr IX, Mn X).
[6] J. E. Ruedy, Phys. Rev. **44**, 757 (1933).
[7] I. S. Bowen, Rev. Mod. Phys. **8**, 78 (1936).
[8] I. S. Bowen and A. B. Wyse, Lick Obs. Bull. **19**, No. 495 (1939).

line and use as mean λ5191.4, the figures for A III in the Table II are obtained. It should be possible to check the new identification of ^1S in A III through combinations in the extreme ultraviolet.

The A III identification permits a reliable interpolation for K IV. Through the identification of two lines in Ekefors' list as shown in Table III a value for $s^2p^4\,^1S$ is found, which agrees perfectly with the isoelectronic comparison.[9] For $^1S-^1D$ follows $\lambda_{air}4511.0$, which might explain the faint line in the nebulae *NGC* 7027 λ4511.8? (1) and *NGC* 7662 λ4510.8 (0.5).[8]

Figure 1 shows the variation in the observed Slater ratio for $3s^23p^4$ and $3s^23p^2$. In order to allow a direct comparison with the theoretical formulae for intermediate coupling, we follow Robinson and Shortley's very useful methods[10] and plot the ratio against the parameter χ as determined from the coupling ratios $(^3P_2-^3P_0):(^1D-^3P_c)$ and $(^3P_1-^3P_2):(^1D-^3P_c)$ for p^2 and p^4, respectively. It should be noticed that the

TABLE III. K IV.

Combination	ν calc.	ν obs.	λ obs.
$s^2p^4\,^1S_0-sp^5\,^1P_1$	132592	132591.9	754.194 (3?)
$-(^2P)4s\,^3P_1$	254925	254923.9	392.274 (2)
$-3d\,^1P_1$	222897	—	masked
$-(^2P)4s\,^1P_1$	259586	—	absent

[9] A previous tentative location of ^1S in K IV by H. A. Robinson and G. H. Shortley [Phys. Rev. **52**, 725 (1937)] repeated by Wei-Zang Tsien [Chinese J. Phys. **3**, 117 (1939)] admits too large errors for Ekefors' measurements and involves an impermissible deviation in the isoelectronic comparison.

[10] H. A. Robinson and G. H. Shortley, Phys. Rev. **52**, 713 (1937). Two minor errors in Tables I and II of this reference were corrected while constructing the theoretical curves in Fig. 1.

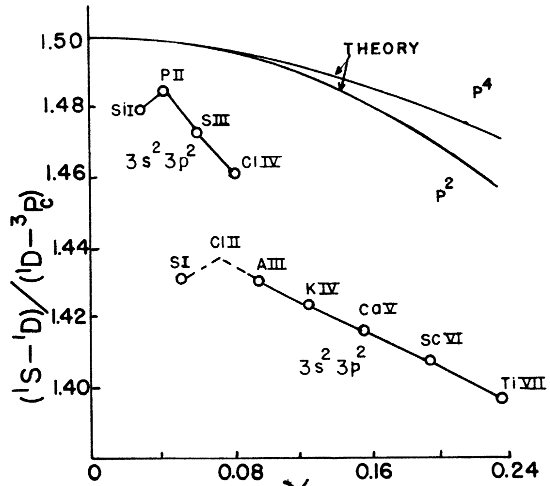

FIG. 1. The Slater ratio $(^1S-^1D):(^1D-^3P_c)$ as a function of the coupling parameter $\chi=\zeta_p/5F_2$.

scale used for Fig. 1 is such that an error in the position of ^1S of less than 50 cm^{-1} would cause an easily recognized discontinuity in the smooth curve from Ti VII to A III. By assuming now a drop in the Slater ratio from Cl II to S I, similar to that observed from P II to Si I, the ratio 1.437 for Cl II may be obtained from the diagram, corresponding to 27900 cm^{-1} as predicted position for ^1S. The published tables of the chlorine spectrum are, however, insufficient for a further confirmation. Kiess and de Bruin[1] were also unable to find the term in spite of careful examination of various unpublished lists. It seems inevitable to assume that $3s^23p^4\,^1S$ has only quite few and comparatively faint combinations, at least for the first elements in the S I sequence.

COMMENTS

I am indebted to the author of this article for the opportunity to comment upon it. It is clear from his data that my earlier identification of λ769.152 was incorrect, as were my values of the $s^2p^4\,^1S_0$ and $sp^5\,^1P_1{}^0$ terms based upon it. A re-examination of unpublished argon lists in the vacuum ultraviolet gives no evidence of the $s^2p^4\,^1S_0-sp^5\,^1P_1{}^0$ line in A III or of other lines which might serve to locate the $^1S_0$ term of the ground configuration. A similar re-examination by C. C. Kiess of unpublished lists of chlorine gives the same negative result for Cl II and confirms the conclusion that lines to the $^1S_0$ state must be relatively faint.

Line lists and term values in A III already published* must now be revised. In addition to the change indicated above, previous identifications of the lines λ1205.95, λ676.241, and λ623.767 must now be withdrawn, as well as the tentative ones for λ604.152 and λ536.745. The four intersystem combinations locating the $s^2p^4\,^1D_2$ term relative to the triplet system are in no way affected by this revision.

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* J. C. Boyce, Phys. Rev. **48**, 396 (1935); **49**, 351 (1936).