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The Configurations $(3d+4s)^n\,4p$ in Neutral Atoms of Calcium, Scandium, and Titanium*

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Experimental levels of the configurations $(3d+4s)^n\,4p$ for neutral atoms of calcium, scandium, and titanium were compared with corresponding calculated values. The rms errors in the calculated values for Ca I, Sc I and Ti I were 23, 126, and 261 cm^{-1}, respectively.

Key words: Configurations $(3d+4s)^n4p$; energy levels; first spectra; g-factors; interactions between configurations; iron group.

1. Introduction

Racah and Shadmi [1, 2][1] investigated the configurations $3d^n+3d^{n-1}4s$ in the second and third spectra of the iron group. The configurations $3d^n4p$ in the second and third spectra of the iron group, the configurations $3d^n4p+3d^{n-1}4s4p$ for Sc II, Ti II and V II, as well as the odd configurations of Cu II were investigated by the author [3−6][2].

For neutral atoms of the iron group the only configurations previously investigated were $(3d+4s)^34p$ —Ti I by Rohrlich [7]. However, Rohrlich considered this spectrum in the $L-S$ approximation by taking into account only the interaction between the cores $3d^3$ and $3d^24s$, and that just as a perturbation to the calculated terms. Although for the final result Rohrlich obtained the very high rms error of 1109 cm^{-1}, most of his parameters were taken as starting values for the present investigation. Mainly for this reason the spectrum of titanium was considered first.

2. Ti I —$(3d+4s)^34p$

The configurations $(d+s)^3p$ comprise 92 theoretical terms splitting into 212 levels. In AEL [8], 74 terms splitting into 175 levels are assigned to the configurations $3d^34p+3d^24s4p$. In addition, 11 odd terms splitting into 28 levels are given without a definite configuration designation in AEL. However, in the original paper by Russell [9], only the term $w\,^1$G is given with no configuration designation. Russell suggests that the terms $w\,^3$H, $p\,^3$D, $t\,^3$G, $q\,^3$F, and $n\,^3$D with no configuration designation in AEL, may be attributed to configurations containing a $5p$ electron. The terms $s\,^3$F, $q\,^3$D, and $v\,^1$D Russell assigns as $3d^3(b^2\mathrm{D})p\,s^3$F, $3d^3(b^2\mathrm{D})p\,q^3$D and $3d^3(a^2P)p\,v^1$D and $3d^24s(a^2\mathrm{S})4p\,t^3P$ of AEL to the configuration $3d4s^24p$.

Rohrlich also assigns the terms t^3P, o^3D and r^3F to the configuration $3d4s^24p$. In addition, he attributes the singlets v^1D at 43710 and $u\,^1$F at 48365 to $3d4s^24p$.

2.1. Initial Parameters

Considering the three configurations $3d^34p$, $3d^24s4p$, and $3d4s^24p$ we obtain [3] from Rohrlich initially:

$$\begin{aligned} A &= 37880 \\ A' &= 30650 \\ A'' &= 45130 \\ B=B' &= 563 \\ C=C' &= 2122 \\ F_2=F_2'=F_2'' &= 281 \\ G_1=G_1'=G_1'' &= 306 \\ G_3=G_3'=G_3'' &= 0 \\ G_{ds}' &= 1381 \\ G_{ps}' &= 4834 \end{aligned} \tag{1}$$

As did Rohrlich, we made the intitial assumption that the values of the parameters B, C, F_2, G_1, and G_3 are the same for the three configurations. The initial

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[1] Figures in brackets indicate the literature references at the end of this paper.
[2] The reader is referred to these papers for an explanation of the method used, notation and significance of the various parameters.
The numerical values of all levels and parameters are in cm^{-1}.
[3] Unprimed quantities refer to the configuration $3d^n4p$, primed quantities to $3d^{n-1}4s4p$ and doubly primed quantities to $3d^{n-2}4s^24p$.

values of the parameters α, J, and K were taken from V II $-3d^34p+3d^24s4p$ [5]

$$x=\alpha'=55$$
$$J'=J=1011 \tag{2}$$
$$K'=K=3288$$

Here α is the average of α and α' in V II.

From the results of Ti II, V II and Cu II [5], [6], we would expect that the parameter H should have the same sign as J and K. Nevertheless, initially two diagonalizations were performed equal in all respects except for changes in the sign of H. The initial numerical value of 100 was also taken from Rohrlich.

As the effect of the interaction between the configurations $3d^34p$ and $3d^24s4p$ depends on the difference between the heights of these two configurations, the value of A' in (1) was checked by considering as for V II $-3d^34p+3d^24s4p$ [5], the terms ^{5}F and ^{5}G whose electrostatic interaction matrices are of order 2. The electrostatic matrix of ^{5}F was given for V II [5], whereas the electrostatic matrix of ^{5}G is

$$\begin{bmatrix} A-15B-F_2-10G_1-10G_3+12\alpha & \dfrac{\sqrt{5}}{5}(K-J) \\ \dfrac{\sqrt{5}}{5}(K-J) & A'-8B'-2G'_{ds}+F'_2-9G'_1-4G'_3-G'_{ps}+12\alpha' \end{bmatrix}$$

Then, by using the centers of gravity for z^5G, z^5F, y^5G, and y^5F, which are 16202, 17046, 26726, and 28767 [8], respectively, we obtain values of A and A', which, in both cases are close to the values of these parameters in (1).

From the small splittings of the terms we note that the spin-orbit interaction is small compared with the electrostatic interaction, [8]. Furthermore, the decomposition of each term into the multiplet levels obeys in general Lande's interval rule. Thus, in order to simplify the initial analysis, we considered first the L-S approximation.

2.2. Discussion and Results

As G'_{ps} is much larger than G'_{ds}, the interaction $p-s$ is stronger than the interaction $d-s$. Thus, the terms of the configuration d^2sp are coupled as

$$d^2(v_1S_1L_1)sp(^{1,3}\mathrm{P})SL$$

and not $d^2s(S_2L_1)p\ SL$ as given in AEL.

Besides the large rms error obtained by Rohrlich, a very disturbing feature of his analysis, is the rejection of six terms, four of which are below 40,000. The experimental terms $y\,^1$D at 27907 and $w\,^3$F at 33683 (note misprint of v instead of w on p. 1384 of Rohrlich [7]), are rejected since they show the very high deviations of 3386 and -3307, respectively. For the experimental terms $u\,^3$F at 37769 and $t\,^3$D at 38721, there are no corresponding calculated terms. However, from an examination of the combinations given by Russell, [9], we obtain the results in table 1 (using the notation for the terms of AEL).

TABLE 1. *Observed transitions from* y ^{1}*D*, w ^{3}*F*, u ^{3}*F*, *and* t ^{3}*D*

Term	Combines with	Number of combinations
$y\,^1$D	$a\,^3$F, $a\,^3$P, $a\,^1$D, $e\,^1$D	4
$w\,^3$F	$a\,^3$F, $b\,^3$F, $a\,^3$G, $a\,^3$D	19
$u\,^3$F	$a\,^3$F, $a\,^1$D, $a\,^3$P, $b\,^3$F, $a\,^3$G, $a\,^3$D	22
$t\,^3$D	$a\,^3$F, $a\,^1$D, $a\,^3$P, $b\,^3$F, $a\,^3$D, $a\,^3$P	21

As all four terms are too low to be assigned to configurations containing a $5p$ electron, they must be valid terms of $(3d+4s)^34p$. Thus, initially terms above 40,000 were not inserted into the least-squares in attempts to obtain suitable parameters so that all the lower-lying terms should fit. Since, with the parameters of (1) and (2), the lowest term of ds^2p is at around 43,500, it was necessary to keep A'' fixed at the initial value of 45,130.

From the least-squares fitting performed on the first two diagonalizations (with H positive and negative) it was evident that H should be in phase with J and K.

The agreement bewteen the experimental and calculated terms was steadily improved from iteration to iteration by letting the parameters B, C, and F_2 differ for the configurations d^3p and d^2sp. Among the terms still showing high deviations were y^1D, w^3F, u^3F, and $t\,^3$D with deviations of around -1400, -800, -700, and -550, respectively. However, an examination of the theoretical compositions of these terms revealed that their eigenfunctions contained a considerable mixture of ds^2p. Thus a diagonalization was performed so that A'', the height of ds^2p, should have a value of 41,000 instead of the original 45,130. As expected, the deviations for the terms $y\,^1$D, $w\,^3$F, $u\,^3$F, and $t\,^3$D were greatly reduced (with the new A'', the largest deviation of the four terms was -350, for $y\,^1$D). Furthermore, the terms $w\,^3$D at 29814, $y\,^1$P at 35095, and $x\,^1$F at 37623 had deviations of around -500, -700, and -1300, respectively, with A'' fixed at the initial value of 45,130. With the new value of A'', these deviations were reduced to -160, -180, and -250, respectively. Although the term $v\,^3$P at 40,429 was not inserted in the initial least squares, it was apparent that had it been inserted, the resulting deviation would have been around -1000. However, after changing the height of ds^2p and inserting terms up to 44,000, the deviation for $v\,^3$P was 250, since with the new A'', the main contribution to $v\,^3$P is $ds^2p\,^3$P.

In the next variation the parameters J' and K' were allowed to change freely. The rms error was reduced from 342 to 290 with the following parameters of the interaction between configurations:

$$
\begin{aligned}
H &= H' = 172 \pm 4 \\
J &= 1128 \pm 41 \\
J' &= 1874 \pm 87 \\
K &= 2595 \pm 49 \\
K' &= 4392 \pm 157 \\
G &= G'_{ds} = 1554 \pm 37
\end{aligned}
\tag{4}
$$

However, by keeping J and J' equal and letting K' change freely the rms error was increased only to 296. Variations in which G'_1, G'_3, α', and H' were allowed to change freely did not improve the results. Finally, by inserting the parameters of the spin-orbit interaction the rms error was reduced to 261.

In order to ascertain whether a general treatment for the configurations $(d+s)^n p$ of the first spectra is feasible, it is first necessary to obtain all the results under the same conditions. Theoretical investigations of the configurations $(3d+4s)^n 4p$ for all neutral atoms of the iron group were performed. Originally it was hoped that the final parameters would be linear functions of the atomic number analogous to the situation prevailing for singly and doubly ionized atoms [3], [4]. After examining the results of all the spectra investigated,[4] it was decided to have the parameters A, A', A'' (wherever there are levels of the configuration $d^{n-2}s^2p$), G'_{ds}, and G'_{ps} change freely. The parameters B, C, F_2, and G_1 were in arithmetic progression for the three configurations, i.e., $B'-B=B''-B'$, etc. The parameters G_3, α, ζ_d, and ζ_p were kept equal for the three configurations. For the parameters of the interactions between configurations H' was kept equal to H, J' to J, and G to G'_{ds}.

From the results of Sc, Ti, and Fe it was found that K' and K should be different with approximately

$$K'\ (d^{n-1}sp - d^{n-2}s^2p) = K(d^n p - d^{n-1}sp) + 380 + 64n.$$

The parameters β and T had no significance here.

In the least squares of the final iteration in the uniform treatment, 68 experimental terms splitting into 169 levels were fitted by means of 18 free electrostatic parameters and 2 free spin-orbit interaction parameters to yield an rms error of 261. The final parameters with their standard errors are given in table 2.

Below 44,000 cm^{-1} there are 76 experimental terms splitting into 185 levels in AEL. The following 8 terms, which split into 16 levels, were rejected in the final least-squares:

1. $3d^24s(b\,^2P)4p\ y\,^3S$ at 35439
2. $w\,^1G$ at 40883
3. $3d^3(a\,^2H)4p\ u\,^3G$ at $41268_{C.G.}$
4. $w\,^3H$ at $41900_{C.G.}$
5. $p\,^3D$ at $42300_{C.G.}$
6. $3d^24s(a\,^2S)4p$: $w\,^1P$ at 42927
7. $r\,^3F$ at $43625_{C.G.}$
8. $v\,^1D$ at 43710

From table 5, the calculated value of the term $^3P(^1P)y\,^3S$ is 34,002. Thus, if the experimental term $y\,^3S$ were inserted into the least-squares calculations, the deviation would be around 1400. As this deviation is much higher than for the other terms and, furthermore, since the term $y\,^3S$ has combinations only with the two terms $a\,^3P$ and $b\,^3P$ [9], it was not included in the final least-square calculations.

Russell does not attribute to $w\,^1G$ any definite configuration designation and, furthermore, mentions that "this term depends only on three faint lines and may not even be real." This conclusion seems to be verified by our results since to all the calculated levels in the vicinity of $w\,^1G$ there correspond other experimental levels.

From the combinations found by Russell for the levels of $u\,^3G$, it is apparent that $u\,^3G$ is a valid term. However, if assigned to the theoretical term $(^2H)^3G$, the deviation would be around -1300. As this deviation is considerably higher than for the other terms and since the experimental term $u\,^3G$ is high enough in order to conceivably belong to $(3d+4s)^3 5p$, it was not included.

As the three theoretically predicted terms ^3H of $(3d+4s)^3 4p$ correspond to $z\,^3H$, $y\,^3H$, and $x\,^3H$, the term $w\,^3H$ is superfluous. Russell suggests that the terms $w\,^3H$ may be assigned to configurations containing a $5p$ electron. However, in the configurations $(3d+4s)^3 4p$, the term $3d^24s(b\,^2G)4p\ z\,^3H$ at $31{,}930_{C.G.}$ is higher by 13,330 than the term $3d^24s(a\,^4F)4p\ z\,^5D$ at $18{,}600_{C.G.}$. Thus, $w\,^3H$ cannot be assigned to $3d^24s(b\,^2G)5p\ w\,^3H$, since the experimental term $3d^24s(a\,^4F)5p\ v\,^5D$ is higher than $w\,^3H$, [8]. Thus the levels of $w\,^3H$ probably belong to $3d^24s(a\,^4F)5p\ x\,^5G$.

In the vicinity of 42,000 there is only one theoretically predicted term ^3D. Since the experimental terms $p\,^3D$ and $q\,^3D$ are so close it is impossible to decide which term to consider for $(3d+4s)^3 4p$. However, as Russell suggests that $p\,^3D$ may belong to configurations containing a $5p$ electron, we assigned $q\,^3D$ to the theoretical term at 42,700, whose main contribution is $3d4s^24p\ ^3D$. Rohrlich [7], also did not include the terms $w\,^3H$ and $q\,^3D$ in his investigation.

The terms $w\,^1P$, $r\,^3F$, and $v\,^1D$ would yield very high deviations if inserted into the least-squares. As these terms may conceivably belong to, or be strongly perturbed by configurations containing a $5p$ electron, they were not included. Similar conclusions hold for most terms above 44,000.

In the configurations $(3d+4s)^3 4p$, the lowest 6 terms are $(d^2\,^3F + (sp)\,^3P)\ ^{3,5}D, F, G$. It is conceivable that the terms $u\,^3G$, $w\,^3H$, $v\,^5D$, $p\,^3D$, $r\,^3F$, and $t\,^3G$ belong to the lowest terms of $(3d+4s)^3 5p$, with the following assignments:

$$
\begin{array}{llll}
(^3F+^3P): & z\,^3D(p\,^3D) & z\,^3F(r\,^3F) & z\,^3G(t\,^3G) \\
 & z\,^5D(v\,^5D) & z\,^5F(u\,^3G) & z\,^5G(w\,^3H)
\end{array}
$$

In parentheses are the corresponding terms with a $5p$ electron.

From table 5 it is evident that the purity of most levels is very low. In many cases, the mixing involves

[4] Results to be published soon.

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eigenfunctions of levels of both configurations $3d^3 4p$ and $3d^2 4s4p$, and in some instances even all three configurations. The changes in designation given below were performed. The number in brackets gives the average percentage of the theoretical designation for the term under consideration.[5] A colon after the experimental term indicates that Rohrlich also changed Russell's designation:

1. AEL $d^2s(a\,^4\mathrm{F})p\ y\,^3\mathrm{D}$:$\rightarrow$ $(^4\mathrm{F})\ y\,^3\mathrm{D}$ (36)
2. AEL $d^2s(b\,^4\mathrm{P})p\ z\,^3\mathrm{P}$ $\rightarrow$ $^1\mathrm{D}(^3\mathrm{P})\ z\,^3\mathrm{P}$ (52)
3. AEL $d^3(b\,^4\mathrm{F})p\ x\,^3\mathrm{F}$:$\rightarrow$ $^1\mathrm{D}(^3\mathrm{P})\ x\,^3\mathrm{F}$ (57)
4. AEL $d^3(b\,^4\mathrm{F})p\ x\,^3\mathrm{D}$ $\rightarrow$ $^1\mathrm{D}(^3\mathrm{P})\ x\,^3\mathrm{D}$ (72)
5. AEL $d^3(b\,^4\mathrm{F})p\ y\,^3\mathrm{G}$:$\rightarrow$ $^3\mathrm{F}(^1\mathrm{P})\ y\,^3\mathrm{G}$ (55)
6. AEL $d^2s(b\,^4\mathrm{P})p\ w\,^3\mathrm{D}$:$\rightarrow$ $^3\mathrm{F}(^1\mathrm{P})\ w\,^3\mathrm{D}$ (27)
7. AEL $d^2s(a\,^4\mathrm{F})p\ x\,^3\mathrm{G}$:$\rightarrow$ $^1\mathrm{G}(^3\mathrm{P})\ x\,^3\mathrm{G}$ (71)
8. AEL $d^2s(a\,^2\mathrm{D})p\ v\,^3\mathrm{D}$:$\rightarrow$ $^3\mathrm{P}(^3\mathrm{P})\ v\,^3\mathrm{D}$ (71)
9. AEL $d^2s(b\,^2\mathrm{G})p\ w\,^3\mathrm{G}$:$\rightarrow$ $(^4\mathrm{F})\ w\,^3\mathrm{G}$ (69)
10. AEL $d^2s(a\,^2\mathrm{D})p\ y\,^3\mathrm{P}$:$\rightarrow$ $^3\mathrm{P}(^3\mathrm{P})\ y\,^3\mathrm{P}$ (85)
11. AEL $d^2s(b\,^2\mathrm{P})p\ x\,^3\mathrm{P}$:$\rightarrow$ $(^4\mathrm{P})\ x\,^3\mathrm{P}$ (33)
12. AEL $d^2s(a\,^2\mathrm{D})p\ w^3\mathrm{F}$:$\rightarrow$ $(^4\mathrm{F})\ w\,^3\mathrm{F}$ (53)
13. AEL $d^2s(b\,^2\mathrm{G})p\ z\,^1\mathrm{H}$:$\rightarrow$ $(^2\mathrm{G})\ z\,^1\mathrm{H}$ (58)
14. AEL $d^2s(b\,^2\mathrm{G})p\ x\,^1\mathrm{F}$:$\rightarrow$ $ds^2(^2\mathrm{D})\ x\,^1\mathrm{F}^*$ (25)
15. AEL $d^3(b\,^2\mathrm{D})p\ t\,^3\mathrm{D}$:$\rightarrow$ $(^2\mathrm{P})\ t\,^3\mathrm{D}$ (34)
16. AEL $d^3(a^2\mathrm{P})p\ w\,^1\mathrm{D}$ $\rightarrow$ $ds^2(^2\mathrm{D})\ w\,^1\mathrm{D}^*$ (28)
17. AEL $d^3(a\,^4\mathrm{P})p\ s\,^3\mathrm{D}$ $\rightarrow$ $(\mathrm{A}^2\mathrm{D})\ s\,^3\mathrm{D}$ (56)
18. AEL $d^3(a\,^4\mathrm{P})p\ v\,^3\mathrm{P}$:$\rightarrow$ $ds^2(^2\mathrm{D})\ v\,^3\mathrm{P}^*$ (32)
19. AEL $d^3(a\,^2\mathrm{P})p\ r\,^3\mathrm{D}$ $\rightarrow$ $(^4\mathrm{P})\ r\,^3\mathrm{D}$ (42)
20. AEL $d^3(a\,^2\mathrm{G})p\ y\,^1\mathrm{H}$ $\rightarrow$ $(^2\mathrm{H})\ y\,^1\mathrm{H}$ (47)

Finally, it is instructive to consider the reasons for the greatly improved results we obtained as compared with those of Rohrlich, [7].

Most importantly, as opposed to Rohrlich, we considered all the three configurations as one problem by inserting the interactions between configurations d^3p-d^2sp, d^2sp-ds^2p, and d^3p-ds^2p explicitly. As a result it is not possible to assign an experimental level to one particular theoretical level. Rather the percentage compositions of most of the theoretical eigenvalues contain a mixture of levels belonging to the configurations d^3p and d^2sp, and in some cases even to all the three configurations.

A second reason for the very high rms error obtained by Rohrlich is due to the fact that he attempted to insert too many high-lying terms which either belong to $(3d+4s)^3 5p$, or are strongly perturbed by these configurations. Not only did these high-lying terms show large deviations but, also they caused the parameters of $(3d+4s)^3 4p$ to absorb the perturbations due to configurations containing a $5p$ electron. Thus, also the lower-lying terms assumed unnecessarily high deviations. Excellent examples of this effect are the four low-lying and definitely valid experimental terms of $(3d+4s)^3 4p$, i.e., $y\,^1\mathrm{D}$, $v\,^3\mathrm{F}$, $u\,^3\mathrm{F}$, and $t\,^3\mathrm{D}$, which Rohrlich rejected.

Thirdly, Rohrlich did not include the $L(L+1)$ correction. As in our initial diagonalization α already had a value different from zero, it is not possible to give an exact quantitative evaluation of the effect of this parameter. However, it can be expected from previous investigations on spectra of the iron group [10–12], where α was very important, that here also the results are improved greatly by considering the $L(L+1)$ correction.

Fourthly, the approximation of Rohrlich that all the electrostatic parameters are equal for the three configurations is not reasonable. By letting the parameters B, C, and F_2 to be in arithmetic progression the rms error was reduced from 461 to 342. The final values of the parameters B, B', C, and C' in table 2 are very similar to those obtained by Racah and Shadmi for Ti II $-(3d+4s)^3$, [1]. The conclusion that F_2 and F_2' are different was also obtained for the configurations $3d^n 4p+3d^{n-1}4s4p$ of the second spectra, [5].

The insertion of the spin-orbit interaction, thus treating the configurations in intermediate coupling, had the smallest effect. The rms error was reduced only from 295 to 261. The values of the parameters ζ_d and ζ_p are small, and furthermore ζ_p is not well defined.

Below 44,000 cm^{-1} (the limit of the experimental levels inserted) there are only 7 theoretical levels with no corresponding experimental levels. The lowest of these are the levels $^1\mathrm{D}(^3\mathrm{P})^3\mathrm{P}_0$ and $^3\mathrm{P}(^3\mathrm{P})\,^1\mathrm{S}$ at 25,713 and 26,170, respectively.

It is interesting to note that the experimental levels $r\,^3\mathrm{D}_3$ and $x\,^3\mathrm{S}_1$ have exactly the same numerical value. However, the combinations of these two levels are quite different [9], and hence the fact that they are coincident is quite accidental. Both levels were inserted into the least-squares calculations.

3. Sc I $-(3d+4s)^2 4p$

The configurations $(d+s)^2 p$ comprise 29 theoretical terms splitting into 70 levels. In AEL [8], 26 experimental terms splitting into 63 levels are assigned to the configurations $3d^2 4p+3d4s4p$. Of these, the three levels of the terms $3d^2(a^3\mathrm{P})4p\ v^2\mathrm{D}$ and

$$3d^2(a^3\mathrm{P})4p\ z^2\mathrm{S}$$

are given with an uncertainty of y cm^{-1}.

[5] For the theoretical term designations used the reader is referred to section 5 of this paper.

The initial values of the interaction parameters were taken from the final results of Ti I (these are not exactly the values given in table 2, as the latter were obtained after having all the results of the individual treatments, and then deciding on a uniform treatment). Then, initially,

$$\begin{aligned} B &= 560 \\ C &= 1630 \\ G'_{ds} &= 1650 \\ F_2 &= 150 \\ F'_2 &= 280 \\ G_1 = G'_1 &= 280 \\ G_3 = G'_3 &= 20 \\ G'_{ps} &= 5800 \\ \alpha &= 50 \\ H &= 180 \\ J &= 1500 \\ K &= 3000 \\ \zeta_d = \zeta'_d &= 100 \\ \zeta_p = \zeta'_p &= 110 \end{aligned} \tag{5}$$

The initial value for A was calculated by averaging the values obtained by using the centers of gravity of ^{4}G and ^{2}H, whose electrostatic matrices are of order 1. Then the starting value for A' was obtained by using the result that the trace equals the sum of the eigenvalues on the electrostatic matrices of ^{4}P and ^{4}F, and averaging. Then initially:

$$\begin{aligned} A &= 34658 \\ A' &= 25818 \end{aligned} \tag{6}$$

The term $d^2(^1S)x^2\mathrm{P}_{\mathrm{C.G.}}$ is given at 30,662 in AEL. The classification of the term x^2P is obviously wrong, since the term $d^2(^1S)p\,^2$P is the highest and *not* the lowest term of d^2p (diagonal element: $A+14B+7C-2G_1-7G_3$, [13]). As the terms $z\,^2$P and $y\,^2$P correspond to the two predicted terms ^{2}P of dsp, and furthermore, since the lowest term of d^2p is $(^1\mathrm{D})w\,^2$P, we must assign $x\,^2$P to $4s^24p$. This assignment had already been suggested by Racah [14], who also obtained a value of 24,223 for the unperturbed height of $4s^24p^2$P which we use here initially. Also, initially:

$$\begin{aligned} &J'(s^2p-dsp) = J(dsp-d^2p) = 1500 \quad \text{(HELD EQUAL)} \\ &K'(s^2p-dsp) = K(dsp-d^2p) = 3000 \quad \text{(HELD EQUAL)} \\ &G(s^2p-d^2p) = G'_{ds} = 1650 \quad \text{(HELD EQUAL)} \end{aligned} \tag{7}$$

The only term having a very large deviation in the initial least-squares was $(^1\mathrm{G})w\,^2$F, whose center of gravity is given experimentally at 39,885. (The levels with the uncertainty y cm^{-1} were not considered then). Since the theoretical term $(^1\mathrm{G})^2\mathrm{F}_{\mathrm{C.G.}}$ was calculated at 43,050, and since from the paper by Russell and Meggers [15], we note that each of the levels of $w\,^2$F is based on only the single combination with $a\,^2\mathrm{G}_{7/2}$, the levels of $w\,^2$F were rejected.

After reaching a stage in the investigation when there was no appreciable difference between the values of the parameters in the diagonalization and in the subsequent least squares, a variation was performed by letting J' and K' vary freely. Then the following values for the parameters of the interaction between configurations were obtained:

$$\begin{aligned} H &= 296 \pm 23 \\ J &= 1398 \pm 239 \\ J' &= 1981 \pm 150 \\ K &= 2628 \pm 118 \\ K' &= 3114 \pm 57 \\ G = G'_{ds} &= 1842 \pm 82 \quad \text{(HELD EQUAL)} \end{aligned} \tag{8}$$

As expected, the values of J' and K' are greater than J and K, respectively.

As a consequence of this variation the rms error was reduced from 187 to 118. When J' and K' were held equal to J and K respectively, G_3 and G'_3 assumed small negative values, and thus had to be kept fixed at zero. However, when J' and K' were allowed to vary freely, G_3 and G'_3 had the very reasonable values:

$$\begin{aligned} G_3 &= 13 \pm 5 \\ G'_3 &= 22 \pm 9 \end{aligned} \tag{9}$$

In addition, the agreement of the four experimental Landé g-values was much better after the variation.

Subsequently, a variation was performed by holding J and J' equal and letting K' vary freely. The rms error was only raised to 126, and G_3 as well as G_3' remained positive. This conclusion is similar to those obtained in Ti I and Fe I, where it was also important to have K' free, but J and J' could be equal without impairing the results greatly.[6]

In the least-squares of the last iteration the levels $(^3P)v\,^2D$ are predicted at 42,420 and 42,437, whereas $(^3P)z\,^2S$ was predicted at 35,567. Thus, either the assignments for the levels $(a^3P)p\ v^2D$ and $(a^3P)p\ z^2S$ are not correct, or they cannot be written with a common uncertainty of y cm^{-1}.

The term $u\,^2D$, given in AEL with no configuration assignment most probably belongs to $(3d+4s)^25p$.

Then neglecting the terms $w\,^2F$, $v\,^2D$, $z\,^2S$, and $u\,^2D$, 58 experimental levels were fitted in the individual least-squares to yield a rms error of 126. The parameters with their standard errors obtained in the individual least-squares of the final iteration in the uniform treatments are given in table 2.

As for Ti II$-3d^24p+3d4s4p$, [5], the experimental term $(^1S)^2P$ is missing and thus α has to be kept fixed. Otherwise there would be more parameters than terms to determine them.

Besides the change $d^2(^1S)p\ x\,^2P \leftrightarrow s^2(^1S)p\ x\,^2P$ mentioned previously, the only other change performed was

$$d\,^2D(^3P)z\,^4D_{5/2} \leftrightarrow d\,^2D(^3P)z\,^2D_{5/2}$$

From table 4, comparing the experimental and calculated energy values, we note that there is considerable sharing of eigenfunctions especially between the three doublets $d\,^2D(^3P)z\,^2P$, $d\,^2D(^1P)y\,^2P$, and $s^2(^1S)x\,^2P$.

Below 40,000 cm^{-1}, there are only 4 theoretical levels with no corresponding experimental levels. The lowest of these is the term $(^3P)^2S$ at 35,567.

The agreement between the experimental and calculated g-factors is very good.

4. Ca I $-(3d+4s)4p$

The configurations $(d+s)p$ comprise 8 terms splitting into 16 levels. For $(3d+4s)4p$, [16] all the predicted levels are given in AEL.

The initial values of the interaction parameters were taken from the final results of Sc I (before the uniform treatment):

$$\begin{aligned} F_2 &= 200 \\ G_1 &= 350 \\ G_3 &= 10 \\ G'_{ps} &= 5800 \\ J &= 1700 \\ K &= 3000 \\ \zeta_d &= 60 \\ \zeta_p &= 100 \end{aligned} \tag{10}$$

Initially we tried to obtain the values of A and A' from the matrices of ^1P and ^3P, as for Sc II, [5]. However. the results in the two cases were very different. From ^3P, using the fact that the trace equals the sum of the eigenvalues we obtain

$$A+A'=59{,}560. \tag{11}$$

From the matrix of ^1P:

$$A+A'=52{,}624. \tag{12}$$

Thus the initial value for A was taken as the average of the values obtained by using the centers of gravity of the terms $(dp)^3D$ and $(dp)^3F$. This yields:

$$A=38{,}100. \tag{13}$$

As suggested by Professor Racah, the experimental term $4s(^2S)5p\,^1P$ at 41,679 should be assigned to $3d(^2D)4p\,^1P$.

Then, from the matrix of ^1P

$$A+A'=57{,}571. \tag{14}$$

Now, using (13), (11), and (14), and averaging, we get:

$$A'=20{,}465. \tag{15}$$

The final parameters obtained in the uniform treatment are given in table 2.

When G_3 was left to vary freely, it assumed a value of -5 ± 1. Thus in the final variation G_3 was fixed.

The final values of the parameters J and K, and even G'_{ps}, are quite different than expected on the basis of the results from Sc I and Ti I. This indicates that the configurations $(3d+4s)4p$ are perturbed considerably by $4snp$, $n \geqslant 5$, by $4smf$, $m \geqslant 4$, and by $4d4p$.

The only change in designation was:

$$4s(^2S)5p\,^1P \leftrightarrow 3d(^2D)4p\,^1P.$$

[6] Results to be published soon.

TABLE 2. *Final parameters obtained in the uniform treatment*

Parameter	Ca I$-(3d+4s)4p$	Sc I$-(3d+4s)^2 4p$	Ti I$-(3d+4s)^3 4p$
A	37,936 ± 10	35,511 ± 88	37,749 ± 128
A'	21,128 ± 37	25,085 ± 152	31,989 ± 203
A''		25,616 ± 286	40,514 ± 234
B		529 ± 6	554 ± 7
B'			651 ± 7
C		714 ± 69	1,661 ± 33
C'			2,319 ± 57
$G'_{ds}=G$		1,943 ± 68	1,719 ± 56
F_2	128 ± 2	201 ± 8	153 ± 9
F'_2		284 ± 8	286 ± 8
F''_2			419 (Arith. Progress.)
G_{ps}	4,977 ± 19	5,970 ± 82	5,395 ± 97
G_1	394 ± 2	335 ± 9	283 ± 10
G'_1		327 ± 12	288 ± 10
G''_1			293 (Arith. Progress.)
$G_3=G'_3=G''_3$	0 (Fixed)	5 ± 3	10 ± 3
$\alpha=\alpha'$		50 (Fixed)	43 ± 4
$H=H'$		275 ± 18	175 ± 7
$J=J'$	575 ± 20	1,877 ± 96	1,251 ± 53
K	3,795 ± 32	2,551 ± 95	2,415 ± 48
K'		3,059 (Fixed Diff.)	2,987 (Fixed Diff.)
$\zeta_d=\zeta'_d=\zeta''_d$	18 ± 9	58 ± 21	114 ± 29
$\zeta_p=\zeta'_p=\zeta''_p$	87 ± 16	105 ± 56	114 ± 94
rms error	22.8	126.4	261.4

5. Tables of the Observed and Calculated Levels and *g*-Factors

In the column "NAME" the calculated designation of the term is given. Whenever the terms of the parent d^n have different seniorities these are denoted by the letters A and B, the lower calculated term being designated by A. Whenever a calculated term has a corresponding experimental term the small letters $z, y, x, \ldots$, are used as in AEL. The terms of $d^{n-1}sp$ are denoted by $d^{n-1}v_1S_1L_1(sp^{1,3}\mathrm{P})SL$. The terms of d^np are differentiated from those of $d^{n-2}s^2p$ by using a star for the latter terms.

The entries in the columns "J", "OBS. LEVEL cm^{-1}", "CALC. LEVEL cm^{-1}", are self-evident. In the column "PERCENTAGE" for each calculated level either the three highest contributions or all those contributions exceeding 5 percent are given.

Whenever the experimental and calculated term designations differ, the experimental designation is entered in the column "AEL", using the notation of C. E. Moore, [8]. In many instances, the exchanges involve complete terms rather than isolated levels. Unless specified otherwise, the entries in the column "AEL" pertain to exchanges in terms.

The columns "OBS. g" and "CALC. g" give the observed and calculated values of the g-factors, respectively.

The entries are in ascending order of magnitude of the calculated terms.

TABLE 3. *Observed and calculated levels of* Ca I 3d4p + 4s4p

Name	J	Percentage	AEL	Obs. level (cm^{-1})	Calc. level (cm^{-1})	O–C	Obs. g	Calc. g
$(^2\mathrm{S})^3\mathrm{P}$	0	96		15158	15173	−15		
	1	96		15210	15214	−4		1.500
	2	96		15316	15298	18		1.500
$(^2\mathrm{S})^1\mathrm{P}$	1	$86+14(^2\mathrm{D})^1\mathrm{P}$		23652	23652	0		1.000
$(^2\mathrm{D})^3\mathrm{F}$	2	$87+13(^2\mathrm{D})^1\mathrm{D}$		35730	35726	4	0.754	0.710
	3	100		35819	35807	12	1.076	1.083
	4	100		35897	35889	8	1.245	1.250
$(^2\mathrm{D})^1\mathrm{D}$	2	$87+13(^2\mathrm{D})^3\mathrm{F}$		35835	35877	−42	0.893	0.957
$(^2\mathrm{D})^3\mathrm{D}$	1	100		38192	38176	16		0.501
	2	100		38219	38207	12		1.167
	3	100		38259	38251	8		1.333
$(^2\mathrm{D})^3\mathrm{P}$	0	96		39333	39337	−4		0.000
	1	96		39335	39345	−10		1.499
	2	96		39340	39327	13		1.500
$(^2\mathrm{D})^1\mathrm{F}$	3	100		40538	40556	−18		1.000
$(^2\mathrm{D})^1\mathrm{P}$	1	$86+14(^2\mathrm{S})^1\mathrm{P}$	$4s(^2\mathrm{S})5p\ ^1\mathrm{P}$	41679	41679	0		1.000

TABLE 4. *Observed and calculated levels of* Sc I $(3d+4s)^2 4p$

Name		Percentage	AEL Config.	AEL Desig.	Obs. level (cm^{-1})	Calc. level (cm^{-1})	O − C	Obs. g	Calc. g
$^2D(^3P)z\,^4F$	3/2	99	$3d4s(a\,^3D)4p$	$z\,^4F$	15,673	15,598	75		0.406
	5/2	99			15,757	15,662	94		1.031
	7/2	99			15,882	15,752	130		1.239
	9/2	100			16,027	15,863	163		1.333
$^2D(^3P)z\,^4D$	1/2	99	$3d4s(a\,^3D)4p$	$z\,^4D$	16,010	15,959	51		0.001
	3/2	99			16,022	15,991	31		1.196
	5/2	98	$3d4s(a\,^1D)4p$	$z\,^2D$	16,023	16,045	−22		1.368
	7/2	99	$3d4s(a\,^3D)4p$	$z\,^4D$	16,211	16,126	85		1.428
$^2D(^3P)z\,^2D$	3/2	95	$3d4s(a\,^1D)4p$	$z\,^2D$	16,097	16,362	−265		0.799
	5/2	95	$3d4s(a\,^3D)4p$	$z\,^4D$	16,141	16,348	−207		1.201
$^2D(^3P)z\,^4P$	1/2	$87+5\,^2D(^3P)^2P$	$3d4s(a\,^3D)4p$	$z\,^4P$	18,504	18,641	−137		2.401
	3/2	$86+6\,^2D(^3P)^2P$			18,516	18,644	−128		1.677
	5/2	100			18,571	18,706	−135		1.600
$^2D(^3P)z\,^2P$	1/2	$51+34(^1S)^2P^*+13\,^2D(^3P)^4P$	$3d4s(a\,^1D)4p$	$z\,^2P$	18,711	18,775	−64		0.931
	3/2	$52+32(^1S)^2P^*+13\,^2D(^3P)^4P$			18,856	18,837	19		1.389
$^2D(^3P)z\,^2F$	5/2	94	$3d4s(a\,^1D)4p$	$z\,^2F$	21,033	20,936	97		0.857
	7/2	95			21,086	20,990	96		1.143
$^2D(^1P)y\,^2P$	1/2	$67+21(^1S)^2P^*$	$3d4s(a\,^3D)4p$	$y\,^2P$	24,657	24,606	51		0.667
	3/2	$64+22(^1S)^2P^*$			24,657	24,609	48		1.326
$^2D(^1P)y\,^2D$	3/2	$63+35(^3F)^2D$	$3d4s(a\,^3D)4p$	$y\,^2D$	24,866	24,789	77	0.82	0.807
	5/2	$64+35(^3F)^2D$			25,014	24,925	89	1.17	1.200
$^2D(^1P)y\,^2F$	5/2	$64+27(^3F)^2F$	$3d4s(a\,^3D)4p$	$y\,^2F$	25,585	25,658	−73	0.90	0.857
	7/2	$63+27(^3F)^2F$			25,725	25,771	−46	1.14	1.143
$(^3F)z\,^4G$	5/2	100			29,023	29,102	−79		0.572
	7/2	100			29,096	29,183	−87		0.984
	9/2	100			29,190	29,288	−98		1.172
	11/2	100			29,304	29,416	−112		1.273
$(^1S)x\,^2P^*$	1/2	$34+41\,^2D(^3P)^2P+18(^1D)^2P$	$3d^2(a\,^1S)4p$	$x\,^2P$	30,573	30,576	−3	0.68	0.667
	3/2	$34+40\,^2D(^3P)^2P+19(^1D)^2P$			30,707	30,680	27		1.333
$(^3F)y\,^4F$	3/2	100			31,173	30,990	183		0.400
	5/2	100			31,216	31,043	173		1.029
	7/2	100			31,275	31,115	160		1.238
	9/2	100			31,351	31,206	145		1.333
$(^3F)y\,^4D$	1/2	99			32,637	32,687	−50		0.000
	3/2	99			32,659	32,706	−47		1.199
	5/2	98			32,697	32,740	−43		1.369
	7/2	98			32,752	32,792	−40		1.427
$(^3F)z\,^2G$	7/2	90			33,056	33,109	−53		0.890
	9/2	90			33,151	33,208	−57		1.111
$(^3F)x\,^2F$	5/2	$54+29\,^2D(^1P)^2F$			33,154	33,210	−56		0.865
	7/2	$55+30\,^2D(^1P)^2F$			33,278	33,332	−54		1.143
$(^3P)^2S$	1/2	100				35,567			1.998
$(^3F)x\,^2D$	3/2	$30+28(^3P)^2D+26(^1D)^2D$			33,615	33,597	18		0.801
	5/2	$29+28(^3P)^2D+25(^1D)^2D$			33,707	33,692	15		1.194
$(^1D)^2F$	5/2	$81+15(^3F)^2F$				35,965			0.858
	7/2	$82+14(^3F)^2F$				36,062			1.143
$(^1D)w\,^2D$	3/2	$48+17(^1D)^2P+15(^3F)^2D$			36,934	36,920	14		0.943
	5/2	$66+20(^3F)^2D+13\,^2D(^1P)^2D$			37,040	37,018	22		1.200
$(^1D)w\,^2P$	1/2	$62+17(^3P)^2P+6(^3P)^4D$			37,126	37,148	−22		0.632
	3/2	$48+18(^1D)^2D+14(^3P)^2P$			37,086	37,097	−11		1.189

TABLE 4. *Observed and calculated levels of* Sc I (3d+4s)²4p — Continued

Name	*J*	Percentage	AEL Config.	AEL Desig.	Obs. level (cm⁻¹)	Calc. level (cm⁻¹)	O−C	Obs. *g*	Calc. *g*
$(^3P)x\,^4D$	1/2	94				37,330			0.038
	3/2	98			37,486	37,361	125		1.202
	5/2	99			37,553	37,426	127		1.371
	7/2	98			37,717	37,522	195		1.428
$(^3P)z\,^4S$	3/2	98			38,180	38,478	−298		1.994
$(^3P)y\,^4P$	1/2	100			38,571	38,611	−40		2.666
	3/2	98			38,602	38,653	−51		1.739
	5/2	100			38,658	38,719	−61		1.600
$(^1G)z\,^2H$	9/2	91			39,153	39,157	−4		0.928
	11/2	100			39,249	39,279	−30		1.091
$(^1G)y\,^2G$	7/2	$90+10\,(^3F)^2G$			39,393	39,362	31		0.889
	9/2	$82+9(^1G)^2H+9\,(^3F)^2G$			39,424	39,391	33		1.092
$(^3P)^2D$	3/2	$71+15\,(^3F)^2D$				42,420			0.800
	5/2	$70+15\,(^3F)^2D$				42,437			1.200
$(^1G)^2F$	5/2	$87+10\,^2D(^1P)^2F$				43,400			0.857
	7/2	$87+11\,^2D(^1P)^2F$				43,342			1.143
$(^3P)^2P$	1/2	$67+23\,^2D(^1P)^2P$				44,451			0.667
	3/2	$68+23\,^2D(^1P)^2P$				44,535			1.333
$(^1S)^2P$	1/2	91				48,495			0.667
	3/2	92				48,599			1.333

TABLE 5. *Observed and calculated levels of* Ti I (3d+4s)³4p

Name	*J*	Percentage	AEL Config.	AEL Desig.	Obs. level (cm⁻¹)	Calc. level (cm⁻¹)	O−C	Obs. *g*	Calc. *g*
$^3F(^3P)z\,^5G$	2	100	$3d^24s(a\,^4F)4p$	$z\,^5G$	15,877	15,801	76	0.39	0.334
	3	100			15,976	15,889	87	0.93	0.917
	4	100			16,106	16,005	101	1.15	1.150
	5	100			16,268	16,149	119	1.25	1.267
	6	100			16,459	16,320	139	1.33	1.333
$^3F(^3P)z\,^5F$	1	94	$3d^24s(a\,^4F)4p$	$z\,^5F$	16,817	16,723	94	0.00	0.001
	2	98			16,875	16,780	95		1.000
	3	98			16,961	16,866	95	1.26:	1.250
	4	98			17,075	16,981	94	1.34	1.350
	5	98			17,215	17,124	91	1.42	1.400
$^3F(^3P)z\,^5D$	0	94	$3d^24s(a^4F)4p$	$z\,^5D$	18,463	18,455	8		
	1	94			18,483	18,480	3	1.65?	1.498
	2	94			18,525	18,533	−8	1.50	1.497
	3	93			18,594	18,616	−22	1.49	1.498
	4	94			18,695	18,737	−42	1.51	1.497
$^3F(^3P)z\,^3F$	2	$88+8\,^1D(^3P)^3F$	$3d^24s(a^2F)4p$	$z\,^3F$	19,323	19,343	−20	0.67	0.669
	3	$88+7\,^1D(^3P)^3F$			19,422	19,437	−15	1.07	1.086
	4	$88+7\,^1D(^3P)^3F$			19,574	19,583	−9	1.26	1.252
$^3F(^3P)z\,^3D$	1	$84+8\,^3P(^3P)^3D$	$3d^24s(a\,^2F)4p$	$z\,^3D$	19,938	19,942	−4		0.502
	2	$83+8\,^3P(^3P)^3D$			20,006	20,023	−17	1.16	1.166
	3	$83+8\,^3P(^3P)^3D$			20,126	20,155	−29	1.34	1.332

TABLE 5. *Observed and calculated levels of* Ti I $(3d+4s)^34p$ — Continued

Name	J	Percentage	AEL		Obs. level (cm^{-1})	Calc. level (cm^{-1})	O − C	Obs. g	Calc. g
			Config.	Desig.					
^{3}F(^{3}P)$z\,^3$G	3	95	$3d^24s(a\,^2$F$)4p$	$z\,^3$G	21,470	21,490	−20	0.75	0.751
	4	95			21,589	21,598	−9	1.05	1.050
	5	95			21,740	21,739	1	1.21	1.201
^{3}F(^{3}P)$z\,^1$D	2	86 + 10^{3}P(^{3}P)^{1}D	$3d^24s(a\,^2$F$)4p$	$z\,^1$D	22,081	22,615	−534	1.00	1.000
^{3}F(^{3}P)$z\,^1$F	3	97	$3d^24s(a\,^2$F$)4p$	$z\,^1$F	22,405	22,446	−41	1.00	0.999
^{3}F(^{3}P)$z\,^1$G	4	94	$3d^24s(a\,^2$F$)4p$	$z\,^1$G	24,695	24,683	12	0.97	1.006
^{3}P(^{3}P)$z\,^3$S	1	90 + 7(^{2}P)^{3}S	$3d^24s(b\,^4$P$)4p$	$z\,^3$S	24,921	25,062	−141	1.99	1.988
^{3}P(^{3}P)$z\,^5$S	2	93	$3d^24s(b\,^4$P$)4p$	$z\,^5$S	25,103	25,002	101	1.93	1.984
^{3}F(^{1}P)$y\,^3$F	2	44 + 25(^{4}F)^{3}F + 23^{1}D(^{3}P)^{3}F	$3d^24s(a\,^4$F$)4p$	$y\,^3$F	25,107	25,062	45		0.668
	3	43 + 25(^{4}F)^{3}F + 25^{1}D(^{3}P)^{3}F			25,227	25,177	50	1.06	1.084
	4	41 + 23(^{4}F)^{3}F + 27^{1}D(^{3}P)^{3}F			25,388	25,332	56	1.21 ?	1.246
(^{4}F)$y\,^3$D	1	49 + 34^{3}F(^{1}P)^{3}D	$3d^24s(a\,^4$F$)4p$	$y\,^3$D	25,318	25,639	−321	0.50	0.562
	2	28 + 37^{1}D(^{3}P)^{3}P + 19^{3}F(^{1}P)^{3}D			25,439	25,809	−370	1.17	1.330
	3	32 + 32^{3}P(^{3}P)^{5}D + 24^{3}F(^{1}P)^{3}D			25,644	25,980	−336	1.33	1.391
^{1}D(^{3}P)$z\,^3$P	0	43 + 38^{3}P(^{3}P)^{5}D + 7^{3}P(^{3}P)^{1}S				25,713			
	1	64 + 22^{3}P(^{3}P)^{5}D	$3d^24s(b\,^4$P$)4p$	$z\,^3$P	25,537	25,789	−252	1.50	1.493
	2	49 + 20(^{4}F)^{3}D + 14^{3}F(^{1}P)^{3}D			25,494	25,697	−203	1.47	1.379
^{3}P(^{3}P)$y\,^5$D	0	51 + 32^{1}D(^{3}P)^{3}P	$3d^24s(b\,^4$P$)4p$	$y\,^5$D	25,605	25,746	−141		
	1	65 + 19^{1}D(^{3}P)^{3}P			25,636	25,754	−118		1.457
	2	82 + 6(^{4}F)^{5}D			25,700	25,822	−122		1.470
	3	56 + 19(^{4}F)^{3}D + 13^{3}F(^{1}P)^{3}D			25,798	25,902	−104		1.438
	4	87 + 7(^{4}F)^{5}D			25,927	26,004	−77	1.52	1.495
^{3}P(^{3}P)^{1}S	0	68 + 16(^{2}P)^{1}S + 15^{3}P(^{3}P)^{1}S				26,170			
(^{4}F)y^5G	2	94			26,494	26,614	−120	0.34	0.352
	3	96			26,564	26,701	−137	0.91	0.923
	4	98			26,657	26,817	−160	1.15	1.151
	5	100			26,773	26,961	−188	1.25	1.267
	6	100			26,911	27,130	−219	1.34	1.333
^{1}D(^{3}P)$x\,^3$F	2	58 + 19^{3}F(^{1}P)^{3}F + 13(^{4}F)^{3}F	$3d^3(b\,^4$F$)4p$	$x\,^3$F	26,803	26,729	74	0.66	0.653
	3	57 + 20^{3}F(^{1}P)^{3}F + 14(^{4}F)^{3}F			26,893	26,813	80	1.06	1.081
	4	57 + 20^{3}F(^{1}P)^{3}F + 15(^{4}F)^{3}F			27,026	26,939	87	1.23	1.252
^{1}D(^{3}P)$x\,^3$D	1	78 + 12^{3}P(^{3}P)^{3}D	$3d^3(b\,^4$F$)4p$	$x\,^3$D	27,355	27,366	−11	0.51	0.516
	2	73 + 9^{3}P(^{3}P)^{3}D + 7^{3}P(^{3}P)^{5}P			27,418	27,425	−7	1.17	1.210
	3	64 + 9^{3}P(^{3}P)^{3}D + 19^{3}P(^{3}P)^{5}P			27,480	27,480	0	1.36	1.397
^{3}F(^{1}P)$y\,^3$G	3	56 + 23(^{4}F)^{3}G + 10(^{2}G)^{3}G	$3d^3(b\,^4$F$)4p$	$y\,^3$G	27,499	27,332	167	0.75	0.750
	4	55 + 23(^{4}F)^{3}G + 10(^{2}G)^{3}G			27,615	27,474	141	1.05	1.051
	5	53 + 24(^{4}F)^{3}G + 10(^{2}G)^{3}G			27,750	27,645	105	1.21	1.201
^{3}P(^{3}P)$z\,^5$P	1	97	$3d^24s(b\,^4$P$)4p$	$z\,^5$P	27,666	27,670	−4		2.483
	2	91			27,740	27,739	1		1.788
	3	79 + 16^{1}D(^{3}P)^{3}D			27,888	27,873	15		1.602
^{1}D(^{1}P)$y\,^1$D	2	32 + 26(^{2}D)^{1}D* + 17^{3}P(^{3}P)^{1}D	$3d^24s(a\,^2$D$)4p$	$y\,^1$D	27,907	28,254	−347	0.98	1.000
(^{4}F)$y\,^5$F	1	98			28,596	28,452	144	0.00	0.001
	2	98			28,639	28,509	130	1.01	1.000
	3	98			28,703	28,595	108	1.24	1.250
	4	98			28,788	28,709	79	1.34	1.349
	5	97			28,996	28,852	144	1.40	1.399
^{3}F(^{1}P)$w\,^3$D	1	33 + 24(^{4}F)^{3}D + 11(^{4}P)^{3}D	$3d^24s(b\,^4$P$)4p$	$w\,^3$D	29,661	29,811	−150	0.51	0.545
	2	29 + 21(^{4}F)^{3}D + 15(^{4}F)^{5}D			29,769	29,899	−130	1.16	1.221
	3	20 + 35(^{4}F)^{5}D + 15(^{4}F)^{3}D			29,912	30,012	−100	1.34	1.385

Name	J	Percentage	AEL Config.	AEL Desig.	Obs. level (cm^{-1})	Calc. level (cm^{-1})	O−C	Obs. g	Calc. g
$(^4F)x\,^5D$	0	91			29,829	29,837	−8		
	1	$87+7\,^3P(^3P)^5D$			29,855	29,881	−26	1.46	1.454
	2	$77+6\,^3P(^3P)^5D$			29,907	29,971	−64	1.50	1.445
	3	$55+14\,^3F(^1P)^3D+11\,(^4F)^3D$			29,986	30,110	−124	1.49	1.433
	4	91			30,060	30,124	−64	1.49	1.500
$^1G(^3P)x\,^3G$	3	$70+19\,^3F(^1P)^3G+6(^2H)^3G$	$3d^24s(a\,^4F)4p$	$x\,^3G$	29,915	30,051	−136		0.765
	4	$72+19\,^3F(^1P)^3G+6(^2H)^3G$			29,971	30,086	−115		1.050
	5	$71+19\,^3F(^1P)^3G+6(^2H)^3G$			30,039	30,127	−88	1.19	1.200
$^3P(^3P)v\,^3D$	1	$77+16\,^1D(^3P)^3D$	$3d^24s(a\,^2D)4p$	$v\,^3D$	31,184	30,927	257	0.51	0.502
	2	$68+15\,^1D(^3P)^3D$			31,191	30,937	254	1.17	1.167
	3	$69+14\,^1D(^3P)^3D$			31,206	30,952	254	1.34	1.333
$(^4F)w\,^3G$	3	$70+21\,^3F(^1P)^3G$	$3d^24s(b\,^2G)4p$	$w\,^3G$	31,374	30,993	381	0.75	0.751
	4	$69+22\,^3F(^1P)^3G$			31,489	31,126	363	1.05	1.050
	5	$69+22\,^3F(^1P)^3G$			31.629	31,283	346	1.19	1.200
$^3P(^3P)y\,^3P$	0	$85+7(^2P)^3P$	$3d^24s(a\,^2D)4p$	$y\,^3P$	31,686	31,779	−93		
	1	$85+6(^2P)^3P$			31,726	31,811	−85	1.47	1.499
	2	$85+6(^2P)^3P$			31,806	31,878	−72		1.499
$^1G(^3P)z\,^3H$	4	$85+11(^2G)^3H$	$3d^24s(b\,^2G)4p$	$z\,^3H$	31,830	31,824	6	0.80	0.800
	5	$86+10(^2G)^3H$			31,914	31,891	23	1.04	1.034
	6	$86+10(^2G)^3H$			32,014	31,969	45	1.17	1.167
$^1D(^1P)y\,^1F$	3	$36+44(^2G)^1F+11\,^1G(^1P)^1F$	$3d^24s(a\,^2D)4p$	$y\,^1F$	32,858	32,354	504	0.99 ?	0.999
$^1D(^1P)z\,^1P$	1	$37+29\,^3P(^3P)^1P+25(^2P)^1P$	$3d^24s(a\,^2D)4p$	$z\,^1P$	33,661	33,083	578	0.94?	1.010
$(^4P)x\,^3P$	0	$33+34\,^3P(^1P)^3P+20(^2P)^3P$	$3d^24s(b\,^2P)4p$	$x\,^3P$	33,085	33,405	−320		
	1	$33+34\,^3P(^1P)^3P+20(^2P)^3P$			33,091	33,422	−331	1.46	1.495
	2	$34+34\,^3P(^1P)^3P+20(^2P)^3P$			33,114	33,438	−324	1.46	1.500
$(^4F)w\,^3F$	2	$54+30\,^3F(^1P)^3F$	$3d^24s(a\,^2D)4p$	$w\,^3F$	33,656	33,580	76	0.66	0.667
	3	$53+30\,^3F(^1P)^3F$			33,680	33,702	−22	1.09	1.083
	4	$53+30\,^3F(^1P)^3F$			33,701	33,853	−152	1.26	1.250
$^3P(^1P)^3S$	1	$62+37(^4P)^3S$				34,002			1.989
$^1G(^3P)v\,^3F$	2	$81+9(^2D)^3F$*	$3d^24s(b\,^2G)4p$	$v\,^3F$	33,981	34,209	−228	0.63	0.674
	3	$83+9(^2D)^3F$*			34,079	34,198	−119	1.10	1.083
	4	$84+8(^2D)^3F$*			34,205	34,182	23	1.23	1.250
$^3P(^3P)x\,^1D$	2	$56+12\,^3F(^3P)^1D+10\,^1D(^1P)^1D$	$3d^24s(b\,^2P)4p$	$x\,^1D$	35,035	34,517	518		0.993
$(^2G)z\,^1H$	5	$58+26(^2H)^1H+16\,^1G(^1P)^1H$	$3d^24s(b\,^2G)4p$	$z\,^1H$	34,700	34,871	−171	1.02	1.000
$^3P(^3P)y\,^1P$	1	$54+26\,^1D(^1P)^1P+14(^2D)^1P$*	$3d^24s(b\,^2P)4p$	$y\,^1P$	34,947	35,098	−151		1.005
$(^2G)y\,^3H$	4	$84+13\,^1G(^3P)^3H$			35,454	35,247	207	0.79	0.801
	5	$85+12\,^1G(^3P)^3H$			35,560	35,369	191	1.04	1.033
	6	$85+12\,^1G(^3P)^3H$			35,685	35,515	170	1.17	1.166
$(^4P)w\,^5D$	0	99			35,503	35,481	22		
	1	99			35,528	35,506	22	1.51	1.499
	2	99			35,577	35,557	20	1.53	1.499
	3	99			35,653	35,639	14	1.46	1.499
	4	99			35,758	35,757	1	1.46	1.499
$^1G(^1P)y\,^1G$	4	$45+32(^2G)^1G+21(^2H)^1G$	$3d^24s(b\,^2G)4p$	$y\,^1G$	36,000	35,750	250	1.00	1.000
$(^4P)y\,^5P$	1	97			36,298	36,308	−10	2.47	2.491
	2	97			36,341	36,367	−26	1.81	1.830
	3	98			36,415	36,455	−40	1.66	1.665
$(A^2D)w\,^3P$	0	$35+35(^4P)^3P+23(^2P)^3P$			37,091	37,065	26		
	1	$36+35(^4P)^3P+23(^2P)^3P$			37,173	37,181	−8	1.53	1.499
	2	$33+33(^4P)^3P+21(^2P)^3P$			37,325	37,362	−37	1.48	1.531

TABLE 5. *Observed and calculated levels of* Ti I $(3d+4s)^3 4p$ – Continued

Name	J	Percentage	AEL		Obs. level (cm^{-1})	Calc. level (cm^{-1})	O–C	Obs. g	Calc. g
			Config.	Desig.					
$(^4P)y\,^5S$	2	90			37,359	37,178	181	1.99	1.964
$^3P(^1P)u\,^3D$	1	$42+17(^2P)^3D+13(^4P)^3D$	$3d^24s(b\,^2P)4p$	$u\,^3D$	37,852	37,551	301	0.53	0.508
	2	$41+17(^2P)^3D+14(^4P)^3D$			37,977	37,617	360	1.14	1.168
	3	$39+17(^2P)^3D+15(^4P)^3D$			38,160	37,691	469	1.35	1.380
$(^2G)v\,^3G$	3	$77+7\,^1G(^3P)^3G+5(^4F)^3G$			37,555	37,583	−28	0.77	0.782
	4	$81+7\,^1G(^3P)^3G+5(^4F)^3G$			37,618	37,644	−26	1.05	1.058
	5	$85+7\,^1G(^3P)^3G+6(^4F)^3G$			37,690	37,740	−50	1.20	1.199
$(A\,^2D)u\,^3F$	2	$49+20(^2G)^3F+10(^2D)^3F^*$			37,655	37,699	−44	0.65	0.681
	3	$26+14(^2G)^3F+14(^2D)^1F^*$			37,744	37,772	−28	1.08	1.028
	4	$41+26(^2G)^3F+10(^2D)^3F^*$			37,852	37,941	−89	1.24	1.239
$(^2D)x\,^1F^*$	3	$25+16\,^1G(^1P)^1F+13\,^1D(^1P)^1F$	$3d^24s(b\,^2G)4p$	$x\,^1F$	37,623	37,841	−218	0.94	1.042
$(^2P)z\,^1S$	0	$80+18\,^3P(^3P)^1S$			38,201	38,060	141		
$(^2G)x\,^1G$	4	$50+29(^2H)^1G+18\,^1G(^1P)^1G$			38,960	38,200	760	1.02	1.001
$(^2P)t\,^3D$	1	$37+22(^2D)^3D^*+21(^4P)^3D$	$3d^3(b\,^2D)4p$	$t\,^3D$	38,654	38,436	218	0.54	0.503
	2	$32+20(^2D)^3D^*+20(^4P)^3D$			38,700	38,558	142		1.153
	3	$32+20(^2D)^3D^*+22(^4P)^3D$			38,765	38,659	106	1.32	1.329
$(^2H)z\,^3I$	5	100			38,573	38,454	119	0.81	0.834
	6	100			38,669	38,564	105	1.02	1.024
	7	100			38,780	38,691	89	1.15	1.143
$(^2D)w\,^1D^*$	2	$28+30(^2P)^1D+24(A\,^2D)^1D$	$3d^3(a\,^2P)4p$	$w\,^1D$	39,266	38,764	502	1.06	1.005
$(^2H)x\,^3H$	4	93			39,116	39,152	−36	0.882	0.802
	5	$85+12\,^1G(^3P)^3H$			39,152	39,201	−49	1.02	1.034
	6	$85+12\,^1G(^3P)^3H$			39,199	39,255	−56	1.18	1.165
$(^2G)t\,^3F$	2	$58+27(A\,^2D)^3F+11\,^3F(^1P)^3F$			38,451	39,257	−806	0.66	0.672
	3	$55+30(A\,^2D)^3F+11\,^3F(^1P)^3F$			38,544	39,330	−786	1.08	1.087
	4	$52+34(A\,^2D)^3F+11\,^3F(^1P)^3F$			38,671	39,428	−757	1.25	1.250
$(A\,^2D)x\,^1P$	1	$73+16(^2P)^1P$			39,078	39,268	−190		1.003
$(A\,^2D)s\,^3D$	1	$54+14(^2P)^3D+10\,^3P(^1P)^3D$	$3d^3(a\,^4P)4p$	$s\,^3D$	39,662	39,696	−34	0.52	0.508
	2	$60+17(^2P)^3D+11\,^3P(^1P)^3D$			39,686	39,774	−88		1.167
	3	$55+20(^2P)^3D+12\,^3P(^1P)^3D$			39,716	39,910	−194	1.31	1.330
$(^2D)v\,^3P^*$	0	$37+23\,^3P(^1P)^3P+18(^4P)^3P$	$3d^3(a\,^4P)4p$	$v\,^3P$	40,370	40,129	241		
	1	$24+30(^2P)^3S+14\,^3P(^1P)^3P$			40,385	40,125	260		1.662
	2	$36+21\,^3P(^1P)^3P+16(^4P)^3P$			40,467	40,265	202		1.497
$(A\,^2D)w\,^1F$	3	$82+7\,^1D(^1P)^1F$			40,303	40,267	36	1.05	1.007
$(^2P)x\,^3S$	1	$57+13(^2D)^3P^*+8\,^3P(^1P)^3P$			40,844	40,286	558		1.827
$(^2H)z\,^1I$	6	99			40,320	40,342	−22	1.03	1.001
$(^2G)v\,^1F$	3	$43+31\,^1D(^1P)^1F+11(^2D)^1F^*$			41,585	41,026	559		1.000
$(^4P)r\,^3D$	1	$44+22(A\,^2D)^3D$	$3d^3(a\,^2P)4p$	$r\,^3D$	40,556	41,115	−559	0.49	0.502
	2	$43+24(A\,^2D)^3D$			40,671	41,172	−501		1.165
	3	$40+25(A\,^2D)^3D$			40,844	41,269	−425		1.328
$(^2H)y\,^1H$	5	$47+41(^2G)^1H+12\,^1G(^1P)^1H$	$3d^3(a\,^2G)4p$	$y\,^1H$	41,040	41,257	−217	1.03	1.001
$(^2D)s\,^3F^*$	2	$66+18(A\,^2D)^3F+6\,^1G(^3P)^3F$		$s\,^3F$	41,337	41,307	30	0.66	0.669
	3	$67+19(A\,^2D)^3F+6\,^1G(^3P)^3F$			41,458	41,441	17	1.09	1.084
	4	$68+18(A\,^2D)^3F+5\,^1G(^3P)^3F$			41,624	41,618	6	1.24	1.250
$(^2P)u\,^3P$	0	$36+36(A\,^2D)^3P+9\,^3P(^1P)^3P$			41,959	41,627	332		
	1	$36+37(A\,^2D)^3P+9\,^3P(^1P)^3P$			41,944	41,605	339		1.500
	2	$38+37(A\,^2D)^3P+9\,^3P(^1P)^3P$			41,929	41,562	367		1.498

TABLE 5. *Observed and calculated levels of* Ti I $(3d+4s)^3 4p$ — Continued

Name	J	Percentage	AEL Config.	AEL Desig.	Obs. level (cm^{-1})	Calc. level (cm^{-1})	O−C	Obs. g	Calc. g
$(^2H)^3G$	3	$89+7\,{}^3F(^1P)^3G$				42,539			0.751
	4	$89+7\,{}^3F(^1P)^3G$				42,553			1.050
	5	$89+7\,{}^3F(^1P)^3G$				42,581			1.199
$(^2D)q\,^3D^*$	1	$39+20\,{}^3P(^1P)^3D+13(^2F)^3D$		$q\,^3D$	42,146	42,621	−475		0.501
	2	$27+14\,{}^3P(^1P)^3D+13(^2F)^1D$			42,207	42,640	−433		1.114
	3	$39+20\,{}^3P(^1P)^3D+14(^2F)^3D$			42,311	42,809	−502	1.32	1.333
$(^2P)^1D$	2	$29+16(^2D)^1D^*+12(^2D)^3D^*$				42,799			1.053
$(^2H)v\,^1G$	4	$30+36(^2F)^1G+29\,{}^1G(^1P)^1G$			43,674	43,534	140	0.95	1.000
$(A^2D)u\,^1D$	2	$38+29\,{}^1D(^1P)^1D+19(^2F)^1D$			43,800	44,256	−456	0.98:	1.001
$(^2P)^1P$	1	$37+29(^2D)^1P^*+12\,{}^3P(^3P)^1P$				44,480			1.000
$(^2D)^1P^*$	1	$51+23\,{}^1D(^1P)^1P+21(^2P)^1P$				44,818			1.008
$^1G(^1P)^1H$	5	$72+27(^2H)^1H$				43,356			1.000
$(^4P)^3S$	1	$59+35\,{}^3P(^1P)^3S$				45,555			1.991
$(^2F)^3F$	2	97				46,744			0.667
	3	$86+11(^2F)^3G$				46,731			1.047
	4	$87+10(^2F)^3G$				46,729			1.229
$(^2F)^3G$	3	$87+11(^2F)^3F$				46,954			0.787
	4	$87+10(^2F)^3F$				46,985			1.071
	5	97				47,002			1.200
$^3P(^1P)^3P$	0	$41+45(^2D)^3P^*$				47,964			
	1	$41+44(^2D)^3P^*$				48,010			1.499
	2	$41+44(^2D)^3P^*$				48,094			1.499
$(^2F)^1F$	3	$48+24(^2D)^1F^*+15\,{}^1G(^1P)^1F$				48,856			1.000
$(^2F)^1D$	2	$67+19(A^2D)^1D+12\,{}^1D(^1P)^1D$				49,337			1.000
$(^2F)^1G$	4	$62+19\,{}^1G(^1P)^1G+19(^2H)^1G$				49,392			1.000
$^1S(^3P)^3P$	0	92				49,646			
	1	91				49,689			1.496
	2	$66+23(^2F)^3D$				49,802			1.406
$(^2F)^3D$	1	$81+11\,{}^3P(^1P)^3D$				49,951			0.504
	2	$58+26\,{}^1S(^3P)^3P+8\,{}^3P(^1P)^3D$				49,886			1.260
	3	$80+9\,{}^3P(^1P)^3D$				49,853			1.333
$^1G(^1P)^1F$	3	$38+41(^2F)^1F+16(^2D)^1F^*$				53,342			1.000
$(B^2D)^1P$	1	$47+43\,{}^1S(^1P)^1P$				56,958			0.949
$(B^2D)^3F$	2	$85+11(B^2D)^3D$				57,040			0.724
	3	$78+18(B^2D)^3D$				57,046			1.129
	4	97				57,101			1.250
$(B^2D)^3D$	1	$86+5\,{}^1S(^3P)^3P$				57,154			0.553
	2	$85+11(B^2D)^3F$				57,162			1.111
	3	$78+18(B^2D)^3F$				57,176			1.287
$(B^2D)^1D$	2	$86+9(^2F)^1D$				57,951			0.999
$(B^2D)^3P$	0	92				58,656			
	1	91				58,612			1.498
	2	91				58,519			1.498
$(B^2D)^1F$	3	93				58,886			1.000
$^1S(^1P)^1P$	1	$48+48(B^2D)^1P$				65,788			1.000

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