

The Classification of the Odd Terms of Ti I

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The odd configurations $3d^24s4p$, $3d^34p$ and $3d4s^24p$ of Ti I are calculated using the results of the preceding paper. Numerical values for the F^k and G^k integrals are found by comparison with the observed levels in a method of successive approximation. A correction is applied for configuration interaction which improves the general agreement.

Explicit formulae are given for the multiplet strengths of transition arrays involving equivalent electrons. They are applied to the transitions d^2sp-d^3s and $d^2sp-d^2s^2$ of Ti I. Tables of multiplet strengths are calculated corresponding to interaction energies diagonal in first-order and second-order eigenfunctions, respectively.

On the basis of these calculations and known measurements of line intensities and gf values, a new classification of the odd terms of Ti I is proposed. Of the 83 observed odd terms, 76 were classified. In 74 cases the calculated terms fit with a mean deviation of $\pm 1023 \text{ cm}^{-1}$ on a range of about $30,000 \text{ cm}^{-1}$. Although the experimental data on multiplet strengths are rather scarce, they seem to be in better agreement with theory when based on the new classification.

I. INTRODUCTION

THE spectra of Ti I and Ti II were analyzed in 1927 by Henry Norris Russell.¹ His classification is based to a large extent on the intensity estimates by A. S. King.² He was able to identify 142 terms in Ti I and 50 terms in Ti II, and thus accounted for 1394 and 529 lines, respectively.

However, whereas the spin, orbital, and total angular momenta of a level can be identified experimentally in a rather reliable manner, it is sometimes very difficult to specify the configuration and the series limit. A number of terms, therefore, were classified on admittedly doubtful arguments, especially in the spectrum of Ti I.

The classification of the even terms of Ti I was shown by Many³ to be in satisfactory agreement with theory. The odd terms will be considered in this paper. Most of the odd terms arise from the configurations $3d^24s4p$, $3d^34p$, and $3d4s^24p$. In these configurations the p electron is bound more weakly than the s electron, so that the excited configurations are of the form $3d^24sm_p$, $3d^3m_p$, and $3d4s^2m_p$ ($m = 5, 6, \dots$) and have as their series limit the even configurations of Ti II. These latter configurations, $3d^24s$, $3d^3$, and $3d4s^2$, were also found to be in agreement

with theory.³ The only doubtful point in the Ti II spectrum was the assignment of the two lowest terms, a^4F and b^4F , which Many assigned to $3d^3$ and $3d^24s$, respectively, contrary to Russell's original assignment. This question remained open until recently when Russell showed conclusively⁴ that the lowest term of Ti II has the configuration d^2s , in agreement with his original assignment.

Since the calculated energy terms are not always conclusive for the purpose of configuration assignments, we had to make use of the experimental data on intensities and line strengths.⁵ It was necessary, therefore, to calculate the multiplet strengths of the most important transition arrays.

The next section will give a brief outline of the numerical methods adopted to find the values of the F^k and G^k integrals which are here simply regarded as parameters. Section III will deal with the resulting term energies and the correction for configuration interaction. Intensities and line strengths are discussed in Section IV, and tables of multiplet strengths are given which are calculated by means of the general formulae derived in the appendix. The last section is devoted to a discussion of the most important aspects of the proposed new classification.

¹ H. N. Russell, *Astrophys. J.* **66**, 347 and 283 (1927).

² A. S. King, *Astrophys. J.* **39**, 139 (1914) and **59**, 155 (1924).

³ A. Many, *Phys. Rev.* **70**, 511 (1946).

⁴ H. N. Russell, *Phys. Rev.* **74**, 689 (1948). Kindly communicated by letter before publication.

⁵ A. S. King and R. B. King, *Astrophys. J.* **87**, 24 (1938).

TABLE I. List of parameters for Ti *I*. Columns 1 and 2 give the parameters as calculated on the basis of the current assignment for d^3p and d^2sp , respectively. Column 3 gives the results under the assumption that some configuration assignments have to be interchanged. Column 4 gives an estimate; columns 5, 6, and 7 list the parameters as found in steps by the method of successive approximation.

	1	2	3	4	5	6	7
$A(d^3p)$	39,240	—	36,732	38,000	38,410	38,290	37,972
$A(d^2sp)$	—	28,291	29,456	29,800	30,651	30,729	30,491
$A(ds^2p)$	—	—	—	45,000	—	—	45,241
B	578	522	577	600	570	573	563
C	1,641	4,259	2,555	2,400	2,193	2,108	2,122
F_2	239	106	40	300	295	293	281
G_1	305	96	256	280	332	315	306
G_3	37	-81	17	20	9	2	0
G_d	—	740	0	1,300	938	1,344	1,381
G_p	—	5,499	4,624	4,000	5,628	5,145	4,834

II. CALCULATION OF THE PARAMETERS F^k AND G^k

The matrices for the term energies of the configurations d^2sp and d^3p were calculated in the preceding paper.⁶ The terms of ds^2p follow immediately from the well-known⁷ terms of dp , since these two configurations differ only by a constant.

In the Ti *I* spectrum the spin-orbit interaction is small compared to the electrostatic interaction, and the decomposition of each term into the multiplet levels is in general well represented by Lande's interval rule. We expect, therefore, that Russell-Saunders coupling is a good approximation and that the above mentioned theoretical term energies should fit the experimental values.

We can further assume that the integrals B , C , F_2 , G_1 and G_3 occurring in the matrices of the three odd configurations are the same for all cases where the principal quantum number is the same. The configurations $3d^24s4p$, $3d^34p$ and $3d4s^24p$ are therefore determined by the ten parameters

$$A(d^2sp), A(d^3p), A(ds^2p), \\ B, C, F_2, G_1, G_3, G_d, G_p.$$

Under these conditions one can easily show that the current assignment of the odd Ti *I* terms cannot be completely correct. For this purpose we equated the traces of the matrices of d^3p to the corresponding sums of observed terms, leaving out those traces which involve unobserved terms. The resulting set of ten weighted

linear equations for the six parameters involved in d^3p were then solved by the method of least squares.⁸ The same was done for d^2sp . The results are listed respectively in Table I, columns 1 and 2. We see that the parameters do not at all agree in the two configurations. Also, from considerations of related spectra like Ti *II*, V *II*, etc., one can estimate the values of the parameters of Ti *I*. These estimates are given in the same table in column 4. A comparison with the parameters listed in columns 1 and 2 shows rather poor agreement. A negative value like that of G_3 of d^2sp (column 2) is of course already excluded by virtue of the postiveness of Slater's integrals.

The odd terms 4sSPDFGH occur in both configurations, d^3p and d^2sp . It seems, therefore, possible that some of these terms have a wrong configuration assignment and that they should be interchanged. We recalculated, therefore, the parameters, this time by equating the sum of the traces of d^3p and d^2sp to the observed values for each of the above terms. The result is given in column 3 and is seen to be in much better agreement with the estimates (column 4). The persisting disagreement of F_2 and of G_d , however, indicates that further corrections will be necessary in addition to interchanges of configuration assignments. On solving the secular equations with the parameters of column 3 we did not obtain satisfactory agreement with the experiments. However, when these secular equations were solved with the parameters of column 4 the agreement was much improved.

We used, therefore, the estimated parameters as a first approximation and tried to improve these values by a method of successive approximation. This method is essentially a repeated application of Schrödinger's first-order perturbation theory. One finds the transformation matrix (or eigenvectors) which diagonalizes the energy matrix when the estimated set of parameters is used. This transformation matrix is then used to diagonalize the energy matrix with unspecified parameters. The diagonal elements of the resulting "nearly diagonal" matrix are then equated to the corresponding observed

⁶ F. Rohrllich, Phys. Rev. **74**, 1372 (1948).

⁷ E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge 1935), p. 200.

⁸ For the standard procedures employed see, e.g., *Handbuch der Physik* (Julius Springer, Berlin, 1928), Vol. III, Chap. 13.

terms, and the obtained set of n linear equations for m ($m < n$) parameters is solved by the method of least squares.⁸ One finds an improved set of parameters with which the whole procedure may be repeated. In our case this process yielded the set of parameters listed in Table I, columns, 5, 6 and 7. For column 5 only those terms were taken into account which involve matrices of order one or two in d^3p and d^2sp . In the calculation of the parameters of column 6 all terms of d^3p and d^2sp were used⁹ and finally the configuration ds^2p was included and the resulting parameters (column 7) were regarded as final. A further improvement of the parameters A , as a result of the interaction of the parent configurations, will be discussed in Section III.

From Table I we see that the convergence of the method of successive approximation seems satisfactory and that the final set of parameters is not too far off the estimated values. We think that the improvement caused by one further iteration will hardly justify the great amount of work involved.

The least square method involved the solution of 25, 32, and 41 simultaneous weighted linear equations for 9, 9, and 10 unknowns, respectively.⁸ This could easily be done on an ordinary calculating machine. For the diagonalization of the matrices of order 4, 5, and 6, and for the evaluation of the eigenvectors, however, we used the Electric Network for the Solution of Secular Equations of R. H. Hughes and E. B. Wilson.¹⁰ With its aid symmetrical secular equations up to order six can be solved and the eigenvectors can be measured. For our purpose the accuracy of the instrument had to be improved from 1 percent to about 0.1 percent for the roots. More precisely, the final accuracy obtained was an average error of 0.1 for all roots up to about 250, on an arbitrary scale. Proper scaling enabled us to have most of our roots lying between 100 and 200 or more. The improvement in accuracy was achieved by better calibration of coils and condensers, and by exact determination of corrections for stray capacities. The latter was done by solving quite a number of test problems.

⁹ Single terms with doubtful assignment were omitted. For closely spaced terms whose assignment may have to be interchanged, the weighted average was used.

¹⁰ R. H. Hughes and E. B. Wilson, Rev. Sci. Inst. 18, 103 (1947).

TABLE II. Odd quintet terms of Ti I. All energy values are in units of cm^{-1} . Columns A and B refer to calculations without and with configuration interaction, respectively.

Observed term	Limit		Calc. A		Calc. B	
	$3d^24s$	$3d^3$	Term	Δ_i	Term	Δ_i
2^6G^o	16202	a^4F	15918	-284	16072	-130
2^6F^o	17046	a^4F	17242	196	17396	350
2^6D^o	18598	a^4F	19085	487	19239	641
2^6S^o	25103	b^4P	24738	-365	24892	-211
3^6D^o	25797	b^4P	25199	-598	25353	-444
3^6G^o	26726	b^4F	26186	-540	26092	-634
2^6P^o	27794	b^4P	26967	-827	27121	-673
3^6F^o	28767	b^4F	28534	-233	28440	-327
2^6D^o	29975	b^4F	29027	-948	28933	-1042
3^6D^o	35654	a^4P	36049	395	35955	301
3^6P^o	36367	a^4P	35699	-668	35605	-762
3^6S^o	37359	a^4P	38846	1487	38752	1393
				$\Delta = \pm 682$		$\Delta = \pm 674$
				$\mu = \pm 1365$		$\mu = \pm 1651$

Also, the routine calibration of the small coils which changed their inductance by about 0.1 percent per week was vital to this accuracy. The eigenvectors were measured with an electronic voltmeter which limited the accuracy to a maximum error of 2 percent. Actually, however, the accuracy of the eigenvectors was about 1 percent in most cases as could easily be checked by their orthogonality relations.

III. TERM ENERGIES AND CONFIGURATION INTERACTION

The term energies calculated with the final set of parameters are listed in Tables II, III, and IV (column A) for the quintet, singlet and triplet system, respectively. The corresponding terms and their limits are shown in the first two sections of Table II for the quintet system, and in the first and third sections of Tables III and IV (assignment II) for the singlet and triplet systems, respectively. Russell's assignment¹ of limits is given in the second section of each table (assignment I). For the quintet system assignment I and assignment II are identical, i.e., Russell's assignment is completely confirmed by the above calculations. In the other two systems quite a number of terms show differences in the two assignments, some in the parent term, some in the parent configuration, and some in both.

We define, as usual, the mean deviation and the mean error in terms of the deviation Δ_i of each term

$$\Delta^2 = \sum \Delta_i^2 / n, \quad \mu^2 = \sum \Delta_i^2 / (n - m),$$

where n is the number of terms and m is the number of parameters which were used to fit these terms.

TABLE III. Odd singlet terms of Ti *I*. The current assignment (due to Russell) is given as *I*, the proposed assignment as *II*. The deviations Δ_i are calculated with respect to assignment *II*. Columns *A* and *B* refer to calculations without and with configuration interaction, respectively. All energy values are in units of cm^{-1} .

Obs. term	Assignment I			Assignment II			Calc. A		Calc. B	
	$3d^24s$	$3d^3$	$3d4s^2$	$3d^24s$	$3d^3$	$3d4s^2$	Term	Δ_i	Term	Δ_i
z^1D^0	22081	a^2F		a^2F			21919	-162	21972	-109
z^1F^0	22405	a^2F		a^2F			21523	-882	21621	-784
z^1G^0	24695	a^2F		a^2F			23964	-731	24054	-641
$1S^0$	—	—	—				26127	—	25771	—
γ^1D^0	27907	a^2D		b^2P			31861	(3954)	31293	(3386)
γ^1F^0	32858		a^2G	a^2D			35385	2527	35211	2353
z^1P^0	33661	a^2D		$b^2P?$			33753	92	33329	-332
z^1H^0	34700		a^2G			a^2G	36756	2056	36490	1790
γ^1P^0	34947	b^2P		$a^2D?$			35749	802	35477	530
x^1D^0	35035	b^2P		a^2D			37356	2321	36827	1792
γ^1G^0	36000		a^2G			a^2G	37350	1350	36817	817
x^1F^0	37623	a^2D				a^2G	37533	-90	37289	-334
z^1S^0	38201		a^2P			a^2P	36776	-1425	37192	-1009
x^1G^0	38960	b^2G		b^2G			38036	-924	38629	-331
x^1P^0	39078		b^2D			b^2_3D	40400	1322	40477	1399
w^1P^{0*}	39266		a^2P			a^2P	37610	-1656	38387	-879
w^1F^0	40303		b^2D			b^2_3D	42323	2020	42260	1957
z^1I^0	40320		a^2H			a^2H	40885	565	40791	471
w^1G^0	40883		?			a^2H	40763	-120	40669	-214
γ^1H^0	41040		a^2H			b^2G	39728	-1312	39859	-1181
v^1F^0	41585	b^2G		b^2G			42771	1186	43075	1490
v^1P^0	42928	$a^2S?$				a^2P	42929	1	43413	485
v^1G^0	43674		a^2H			—	—	—	—	—
w^1D^0	43710		a^2P			c^2D	42356	-1354	42305	-1405
v^1D^0	43800		b^2D			b^2_3D	44912	1112	44236	436
x^1H^0	44163	b^2G				a^2H	41606	-2557	41707	-2456
w^1G^0	46258		$b^2F?$			—	—	—	—	—
$1P^0$	—		—			c^2D	47514	—	47499	—
w^1F^0	48365		$b^2F?$			c^2D	47639	-726	47613	-752
$1D^0$	—		—			b^2F	49139	—	49624	—
$1G^0$	—		—			b^2F	49685	—	49655	—
$1F^0$	—		—			b^2F	51143	—	51105	—
$1P^0$	—		—			b^2F	56392	—	56546	—
$1D^0$	—		—			a^2S	60043	—	60527	—
$1F^0$	—		—			3_1D	61181	—	61299	—
$1P^0$	—		—			3_1D	65146	—	65211	—
							$\Delta = \pm 1358$		$\Delta = \pm 1195$	
							$\mu = \pm 1846$		$\mu = \pm 1624$	

* This term is believed to be $1D^0$.

If we take assignment *II* as a basis, we obtain the differences between observed and calculated term energies as stated in the above-mentioned three tables. We then find for the mean deviations ± 682 , ± 1358 and $\pm 1033 \text{ cm}^{-1}$, and for the mean errors ± 1365 , ± 1846 and $\pm 1225 \text{ cm}^{-1}$, corresponding to the quintet, singlet, and triplet system. All three systems together fit with a total mean deviation of $\pm 1105 \text{ cm}^{-1}$ and with a total mean error of $\pm 1189 \text{ cm}^{-1}$. In these calculations only 74 of the 76 classified terms have been taken into account. The two terms γ^1D^0 and v^3F^0 show much larger deviations than any of the other terms and were therefore omitted in the least-square calculation.

When we consider the interaction between the parent configurations d^3 , d^2s and ds^2 which we

have neglected so far, we may expect improved agreement. The corresponding matrix elements were calculated by Ufford.¹¹ He found that the interaction integral

$$H_2 = (1/35)R^2(dd, ds)$$

is 192 cm^{-1} for Ti *II* whereas Many⁸ found by the least square method 172 cm^{-1} for Ti *II* and 153 cm^{-1} for V *II*. Since Ti *I* and V *II* have the same electron configurations, but the latter has a higher nuclear charge, we expect a still smaller configuration interaction in Ti *I*. A rough estimate of $H_2 = 100 \text{ cm}^{-1}$ turned out to be not much too small.

With this value for the interaction parameter

¹¹ C. W. Ufford, Phys. Rev. **44**, 732 (1933).

TABLE IV. Odd triplet terms of Ti I. For explanation see Table III.

Obs. term	Assignment I			Assignment II			Calc. A		Calc. B	
	$3d^24s$	$3d^3$	$3d4s^2$	$3d^24s$	$3d^3$	$3d4s^2$	Term	Δ_i	Term	Δ_i
z^3F°	19463	a^2F		a^2F			19364	-99	19473	10
z^3D°	20048	a^2F		a^2F			20279	231	20368	320
z^3G°	21619	a^2F		a^2F			21115	-504	21208	-411
z^3S°	24921	b^2P		b^4P			24632	-289	24672	-249
y^3F°	25268	a^4F		a^2D			25761	493	25734	466
z^3F°	25510 ₁₃	b^2P		a^2D			26039	529	26009	499
y^3D°	25510 ₃₄	a^4F		a^2D			26478	968	26452	942
x^3F°	26929		b^4F	a^4F			29029	2100	29137	2208
x^3D°	27434	b^2P			b^4F		27635	201	27527	93
y^3G°	27640		b^4F	a^4F			27370	-270	27524	-116
w^3D°	29814		b^4F	a^4F			30067	253	30137	323
x^3G°	29984	a^4F		b^2G			29433	-551	29470	-514
v^3D°	31197	a^2D		b^2P			30861	-336	30391	-806
w^3G°	31516	b^2G			b^4F		29473	-2043	29379	-2137
y^3P°	31766	a^2D		b^2P			30638	-1128	30407	-1359
z^3H°	31930	b^2G		b^2G			30060	-1870	30052	-1878
x^3P°	33103	b^4P			a^4P		35219	2116	34997	1894
w^3F°	33683	a^2D			b^4F		30470	(-3213)	30376	(-3307)
v^3F°	34109	b^2G		b^2G			33099	-1010	33069	-1040
y^3S°	35439	b^4P		b^2P			35901	462	35428	-11
y^3H°	35580		a^2G		a^2G		35202	-378	35253	-327
w^3P°	37249		a^4P	b^4P			38849	1600	38466	1219
v^3G°	37631		a^2G		a^2G		37421	-210	37444	-187
u^3F°	37769		b^2D							
u^3D°	38037	b^4P		b^4P			37403	-634	37557	-480
t^3F°	38576		a^2G		$a^2G?$		38024	-552	38118	-458
z^3I°	38685		a^2H		a^2H		39049	364	38955	270
t^3D°	38721		b^2F							
x^3H°	39161		a^2H		a^2H		38876	-285	38799	-362
s^3D°	39695		a^4P		a^4P		38774	-921	38872	823
v^3P°	40429		b^2D		a^2P		38843	-1583	39529	-900
r^3D°	40729		a^2P		a^2P		40436	-293	40856	127
x^3S°	40844		a^4P		a^2P		39885	-959	40404	-440
u^3G°	41268		a^2H		a^2H		42391	1123	42297	1029
s^3F°	41500		b^2F		b^2_3D		40670	-830	40423	-1077
u^3P°	41936		a^2P		b^2_3D		42971	1035	43051	1115
q^3D°	42244		b^2D		b^2D		41582	-662	41229	-1015
r^3F°	43625			c^2D		c^2D	43967	342	44012	387
o^3D°	44130			c^2D		c^2D	44192	62	44322	192
w^3S°	44858		a^2P		a^4P		43693	-1165	43727	-1131
t^3P°	45134			c^2D		c^2D	46902	1768	46804	1670
$^3F^\circ$	—				b^2F		47333	—	47329	—
$^3P^\circ$	—			a^2S			47669	—	47893	—
$^3G^\circ$	—				b^2F		48371	—	48338	—
$^3D^\circ$	—				b^2F		50303	—	50291	—
$^3D^\circ$	—				2_1D		58662	—	58765	—
$^3F^\circ$	—				2_1D		59933	—	60014	—
$^3P^\circ$	—				2_1D		61634	—	61735	—
							$\Delta = \pm 1033$		$\Delta = \pm 996$	
							$\mu = \pm 1225$		$\mu = \pm 1182$	

the corrections to the previously calculated term values were found approximately. The corrections are larger for S and P terms. The $^3P^\circ(^2P)$ term of d^3p has the largest correction, viz., 686 cm^{-1} . It is clear that configuration interaction causes in general a shift of the centers of the configurations. These shifts are found by correcting the parameters A so that the sum of the deviations vanishes for each configuration. In the previous calculation the vanishing of this sum was guaranteed by the method of least squares.

The new values for the A 's are

$$\begin{aligned}
 A(d^3p) & 37,878 \text{ cm}^{-1}, \\
 A(d^2sp) & 30,645 \text{ cm}^{-1}, \\
 A(ds^2p) & 45,130 \text{ cm}^{-1}.
 \end{aligned}$$

Using these values instead of those of Table I, column 7, and adding the corrections resulting from configuration interaction to the terms listed in the Tables II, III and IV, column A , one obtains the improved term energies listed in column B of the same three tables. We see that

TABLE V. Observed intensities and multiplet strengths of Ti I (quintet system). The columns *M* and *KK* list intensities (strongest line of each multiplet) and multiplet strengths, respectively. Estimated values are in brackets. The symbols *i*, *m*, *n*, *tr*, *r*, and *R* indicate infra-red, masked, fuzzy lines, trace, narrow, and wide self-reversal, respectively. (See Tables VI and VII.)

Limit	Term	Limit Term	$3d^34s$			
			a^4P a^6P	<i>KK</i>	b^4F a^6F	<i>KK</i>
$3d^24s4p$						
<i>b</i> ⁴ <i>P</i>	z^6S^0		25			
	z^6P^0	(1)				
	y^6D^0		40		6	(5)
<i>a</i> ⁴ <i>F</i>	z^6D^0				300	
	z^6F^0				100	
	z^6G^0				30	
$3d^34p$						
<i>a</i> ⁴ <i>P</i>	y^6S^0		15			
	y^6P^0		30	(440)		
	w^6D^0		30	(450)	4	
<i>b</i> ⁴ <i>F</i>	x^6D^0	(2)			60	637
	y^6F^0				80	802
	y^6G^0				60	(910)

the improvement is considerable. The quintet system is affected only indirectly (by the change of the *A*'s), since there is no interaction between the ⁴*F* terms of the parent configurations.¹¹ The mean deviations are now reduced to ± 674 , ± 1195 and ± 996 cm^{-1} , and the mean errors to ± 1651 , ± 1624 and ± 1182 cm^{-1} for the quintet, singlet, and triplet systems, respectively. The total mean deviation is ± 1023 cm^{-1} , and the total mean error is ± 1109 cm^{-1} .

IV. INTENSITIES AND LINE STRENGTHS

It is well known that the theoretical formulae for the multiplet and super-multiplet analysis are based on relative line strengths whereas the experimenter measures in general intensities. The two differ by the fourth power of the frequency and the Boltzmann factor, which corresponds to a correction to infinite temperature. For multiplet analysis these two corrections can be neglected and one can work with intensities as well as with line strengths. For super-multiplet analysis this is generally not the case, since the separation of the terms which have the same limit is not necessarily negligible with respect to the lines of the transition array, and these lines are not always excited at the same temperature.

However, it seems difficult to find the appropriate corrections for A. S. King's original intensity measurements.² On the other hand, more recent experiments by A. S. King and R. B. King⁵ are much more reliable, both as to homogeneity and to accuracy. Unfortunately, they measured only the strongest multiplets. Their list of *gf* values has to be multiplied by the wave-lengths to obtain line strengths.

In Russell's intensity tables¹ the strongest line (principal line) of each multiplet is given as an indication of the intensity of the total multiplet. In many cases this gives a good relative estimate, but it is not always reliable, and in some cases it seems to distort the picture considerably. In the following, we used, therefore, the sum of the strengths of all the lines of a multiplet to calculate its multiplet strength. If some weak components were not known experimentally, they could easily be estimated from theoretical intensity tables.¹² Usually, this amounted to a correction of not more than 10 percent. In a few cases, however, most of the multiplet strength is due to estimates. These values are given in brackets in Tables V–VII. The columns *M* of these tables list the multiplet intensities, as in Russell's paper, in terms of their principal lines. They include some intensity measurements which were not known to Russell at that time, and some values which are corrected measurements. All these are taken from the Multiplet Tables compiled by Moore,¹³ and are due to various investigators. The multiplet strengths as calculated from the measured *gf* values⁵ are given in the columns *KK* of the same tables. The main differences between the columns *M* and *KK* have to be attributed, therefore—apart from a scale factor—to frequency and temperature corrections. The tables are arranged according to the new assignment.

These Tables (V–VII) of observed multiplet strengths must be compared with Tables VIII–XIII which give the calculated multiplet strengths. The latter are obtained by the following procedure.

The calculation is carried out in two steps. Firstly, we regard the quantum numbers of the

¹² See reference 7, p. 241.

¹³ C. E. Moore, *A Multiplet Table of Astrophysical Interest* (Princeton University Press, Princeton, 1945).

TABLE VI. Observed intensities and multiplet strengths of Ti I (singlet system). In this table the proposed classification is adopted. The meaning of the various symbols is indicated in Table V.

Limit	Term	Limit Term	$3d^24s^2$			b^2G a^2G		a^2P a^1P		b^2D b^1D		$3d^24s$		a^2G b^1G		a^2H a^1H	
			M	M	KK	M	KK	M	KK	M	M	M	M	KK	M	M	
$3d^24s4p$																	
b^2P	z^1P°		20	55				(1)									
	y^1D°		25	22				i									
a^2D	y^1P°	3	12	31				(1)									
	x^1D°		15					(0)									
	y^1F°		40 n	90	20					(2)	i	6					
a^2F	z^1D°		10	3				i									
	z^1F°		12	1	25							i	i				i
	z^1G°				(3)							i	i				
b^2G	v^1F°		40	10						1	(1)	m					
	x^1G°				20	127					i	6					8
	y^1H°				6							8					8
$3d^34p$																	
a^2P	z^1S°							2									
	v^1P°		1	15				3			(2)						
	$w^1P^\circ*$	(1)	15	18				5	859		2						
b^2D	x^1P°	(3)	15	14				(1)			4						
	v^1D°		6					4			7						
	w^1F°		2		15						10	i	(1)				
a^2G	x^1F°		20	35	5					1	i	(0)					
	y^1G°				25						i	18	186				3
	z^1H°				40							20					2
a^2H	w^1G°				m							2					1
	x^1H°				15												7
	z^1I°																12
$3d4s^24p$																	
c^2D	w^1D°		15					5									
	u^1F°		(1)		20						(2)	4					
Unclassified	v^1G°				$2n$						(0)	$2n$					$5n$
	u^1G°				30						(1)	8					10

* This term is believed to be a $^1D^\circ$ term.

parent configurations as "good quantum numbers," and neglect, therefore, the interaction between multiply-occurring terms in each configuration. This amounts to neglecting the off-diagonal elements in the energy matrices calculated in the preceding paper.⁶ The matrices are then diagonal in "first-order eigenfunctions" as defined by Ufford.¹¹ The multiplet strengths can then be calculated with the well-known formulae of Kronig.¹⁴ These formulae are not sufficient, however, in case the jumping electron belongs

to a group of equivalent electrons in one of the configurations. For those cases general formulae are derived in the appendix. With their aid the multiplet strengths of transitions involving equivalent electrons can be calculated from the Kronig strength for transitions not involving equivalent electrons and the coefficients of fractional parentage.^{15,16} The results for the important transition arrays of Ti I are listed in the columns 1 of Tables VIII–XIII.

¹⁵ R. F. Bacher and S. Goudsmit, Phys. Rev. **46**, 948 (1934).

¹⁶ G. Racah, Phys. Rev. **63**, 367 (1943).

¹⁴ Kronig, Zeits. f. Physik **33**, 261 (1925).

TABLE VII. Observed intensities and multiplet strengths of Ti I (triplet system). In this table the proposed classification is adopted. The meaning of the various symbols is indicated in Table V.

Limit	Term	Limit Term	$3d^24s^2$				a^4P c^3P	b^4F b^4F		a^3P b^3P	$3d^24s$		a^2G a^2G		a^2H a^2H		
			M	KK	M	KK		M	M		KK	M	M	M	KK	M	KK
$3d^24s4p$																	
b^4P	z^3S°		20	10	(3)					i							
	w^3P°		12	46						6			8				
	u^3D°		15	52	40				8			1	8				
a^4F	w^3D°		20	24	40 r	75				2	25	136	60				
	x^3F°				80 r	143					25	28		i	100		
	y^3G°				100 r	229				50	145				(4)	10	
b^2P	y^3S°		20	68								2					
	y^3P°		2		tr							(2)	(1)				
	v^3D°		10		5	1			(1)	12	78	(2)	(1)				
a^2D	z^3P°		10	8	40	8				i	5		i				
	y^3D°		35	36	80	104				i	20		i				
	y^3F°				100 R	163					4		(1)	25			
a^2F	z^3D°		150		25	22				i	6		i				
	z^3F°				40	31					i			25			
	z^3G°				30	14					15				i		
b^2G	v^3F°				70 R	(125)				40			$4n$	10	158		
	x^3G°		3		80 R	168				6	(19)		i	(1)	30	180	
	z^3H°				3											75	
																(1)	
$3d^34p$																	
a^4P	w^3S°		6														
	x^3P°		30	105						(1)			(2)				
	s^3D°		6	(36)	20					12	3		(2)				
b^4F	x^3D°		4	9	15	12				2	8		3	(1)			
	w^3F°				20						8			3	6		
	w^3G°				100 R	177					25	315			4	(3)	
a^2P	x^3S°		8										3				
	v^3P°		1							8			4				
	r^3D°		12		(3)					2	8		6	3			
b^2D	u^3P°		tr										8	8			
	q^3D°		15		4						(5)		10				
	s^3F°				10								10	4			
a^2G	t^3F°		2		25						1			15			
	v^3G°				20						2			30		(1)	
	y^3H°													20	429	9	
a^2H	u^3G°				10					2						10 n	
	x^3H°													7		25 (156)	
	z^3I°															20 (334)	
$3d4s^24p$																	
c^3D	t^3P°		30							1			3	1			
	o^3D°		6		12						1						
	r^3F°				12						2				3		
Unclassified																	
	t^3D		15	166	5					15		2	4				
	u^3F°		1		5					3			12	15			

In the second step we do take into account the off-diagonal matrix elements of the multiply-occurring terms of each configuration, but we

still neglect configuration interaction. The energy matrices are now diagonal in "second-order eigenfunctions." The latter are linear combina-

TABLE VIII. Calculated multiplet strengths $d^2s^2p-d^3s$, (quintets).

d^2s	d^2s^2p	d^2s		d^3s	
		1	2	1	2
4P	$^5S^{\circ}$	80	80		
	$^5P^{\circ}$	60	60		
	$^5D^{\circ}$	4	8	126	127
4F	$^5D^{\circ}$	126	122	144	143
	$^5F^{\circ}$			315	315
	$^5G^{\circ}$			45	45
		3×90		7×90	

TABLE IX. Calculated multiplet strengths d^3p-d^3s , (quintets).

d^3	d^3p	d^3		d^3s	
		1	2	1	2
4P	$^5S^{\circ}$	5	5		
	$^5P^{\circ}$	15	15		
	$^5D^{\circ}$	25	24		
4F	$^5D^{\circ}$		1	25	24
	$^5F^{\circ}$			35	35
	$^5G^{\circ}$			45	45
		3×15		7×15	

tions of the first-order eigenfunctions; the corresponding coefficients are the eigenvectors which were measured on the secular equation solver described in Section II. Unfortunately, we do not have these eigenvectors for the even configurations. We have to assume that the first-order eigenfunctions are good enough for them. Under these conditions we obtain the results given in Tables VIII–XIII, column 2. It is important to note that these values are only very rough approximations, since the interactions between the multiply-occurring terms of d^3s are certainly not all negligible (especially in the 3P and 3F terms). Also, we had available only the eigenvectors corresponding to the parameters of Table I, column 6, rather than to the final set of parameters.

Configuration interaction was taken into account only as a correction to the energy terms (cf. Section 3). Therefore, no third-order eigenfunctions are available which would diagonalize all electrostatic interactions, including configuration interaction. It is for this reason that no calculations of apparent two-electron jumps could be made. This affects the transitions $d^3p-d^2s^2$ and ds^2p-d^3s .

V. THE NEW CLASSIFICATION

On the basis of energy terms and multiplet strengths it should be possible to classify all the observed terms of the three deep odd configurations of Ti I. It is mainly due to the relatively small number of measurements of gf values that several assignments remain still uncertain.

The bulk of the classification is based on the calculated terms (Tables II–IV, column B). Although these terms do not always fit the

experimental data very closely, the deviations in most cases are small enough for the identification of the experimental terms, which alone is the final aim of this investigation. On the other hand, there are quite a number of cases where even better agreement would not help very much, because the terms are so closely spaced that the possibility of an interchange of the assignment is not outside the error of the calculation. In these cases one has to rely upon the tables of multiplet strength. For many multiplets, however, only the intensities are measured (columns M of Tables V–VII), whereas no data on multiplet strengths are available. When we compare the intensities (principal lines) with the calculated multiplet strengths we cannot expect more than a rough qualitative agreement in many cases. Only within the theoretical approximations dis-

TABLE Xa. Calculated multiplet strengths $d^2s^2p-d^2s^2$ (singlets).

d^2s	d^2s^2p	d^2s^2		d^2s^2		d^2s^2	
		1	2	1	2	1	2
2S	$^1P^{\circ}$	6	5.9	—	0.1		
2P	$^1S^{\circ}$	—	0.0	—	0.0		
	$^1D^{\circ}$			—	0.5		
2D	$^1P^{\circ}$	—	0.1	6	5.9		
	$^1D^{\circ}$			10	9.4		
	$^1F^{\circ}$			14	13.4	—	0.3
2F	$^1D^{\circ}$			—	0.1		
	$^1F^{\circ}$			—	0.3	—	0.0
	$^1G^{\circ}$					—	0.2
2G	$^1F^{\circ}$			—	0.3	14	13.7
	$^1G^{\circ}$					18	17.8
	$^1H^{\circ}$					22	22.0
		1×6		5×6		9×6	

TABLE Xb. Calculated multiplet strengths $d^2s\bar{p}-d^3s$ (singlets).

d^2s	d^3s	2P		3D		3D		2F		2G		2H	
		1	2	1	2	1	2	1	2	1	2	1	2
2S	$^1P^o$	—	0	24.000	24	—	0						
2P	$^1S^o$	7.00	7.0										
	$^1P^o$	5.25	5.5	10.125	10	23.625	24						
	$^1D^o$	0.35	2.5	3.375	6	7.875	8	50.400	43				
2D	$^1P^o$	20.35	20	2.625	3	10.125	10						
	$^1D^o$	6.75	6	4.375	4	16.875	16	12.000	14				
	$^1F^o$			0.500	1	1.929	2	6.000	6	38.571	38		
2F	$^1D^o$	14.40	13	21.000	19	9.000	9	3.600	9				
	$^1F^o$			10.500	10	4.500	5	7.875	8	50.625	51		
	$^1G^o$							1.125	1	30.375	30	99.00	99
2G	$^1F^o$			13.500	13	16.071	16	28.125	28	10.804	12		
	$^1G^o$							16.875	17	27.225	27	59.40	60
	$^1H^o$									4.400	4	39.60	39
		3×18		5×18		5×18		7×18		9×18		11×18	

cussed in the last section can we expect quantitative agreement, when the measured line strengths are compared. It should be noted that the theoretical and experimental multiplet strengths are in general related by different scale factors for different transition arrays, as is explained in the Appendix.

In order to facilitate the comparison between the observed and the calculated terms, the energies are plotted in Figs. 1-3, for the quintet, singlet, and triplet system, respectively. All terms which have the same S and L value are

TABLE XI. Calculated multiplet strengths, $d^3\bar{p}-d^3s$ (singlets).

d^3	$d^3\bar{p}$	2P		3D		3D		2F		2G		2H	
		1	2	1	2	1	2	1	2	1	2	1	2
2P	$^1S^o$	1	1.0										
	$^1P^o$	3	2.5	—	0.1	—	0.4						
	$^1D^o$	5	3.0	—	0.4	—	1.4	—	0.2				
3D	$^1P^o$	—	0.0	3	2.3	—	0.7						
	$^1D^o$	—	0.0	5	3.1	—	1.2	—	0.8				
	$^1F^o$			7	5.7	—	1.2	—	0.0	—	0.1		
3D	$^1P^o$	—	0.5	—	0.6	3	1.9	—	0.1				
	$^1D^o$	—	2.0	—	0.5	5	2.4	—	0.1				
	$^1F^o$			—	1.3	7	4.7	—	0.1	—	1.0		
2F	$^1D^o$	—	0.0	—	1.0	—	0.0	5	3.9				
	$^1F^o$			—	0.0	—	0.3	7	6.6	—	0.1		
	$^1G^o$							9	7.4	—	0.0	—	1.5
2G	$^1F^o$			—	0.0	—	0.8	—	0.3	7	5.8		
	$^1G^o$							—	0.0	9	8.8	—	0.2
	$^1H^o$									11	7.4	—	3.6
2H	$^1G^o$							—	1.6	—	0.2	9	7.3
	$^1H^o$									—	3.6	11	7.4
	$^1I^o$										—	3.6	13
		3×3		5×3		5×3		7×3		9×3		11×3	

plotted in the same column, so that one can easily interchange the configuration assignments. Each column shows the observed terms together with Russell's limit assignment to the left, and the calculated terms with their limits to the right. The limit assignment gives the term of the parent configuration in brackets, and bears

TABLE XIIa. Calculated multiplet strengths, $d^2s\bar{p}-d^2s^2$ (triplets).

d^2s	$d^2s\bar{p}$	$(2/3)^1P+(1/3)^2P$		$(2/3)^1F+(1/3)^2F$	
		1	2	1	2
2S	$^3P^o$	—	0.4		
2P	$^3S^o$	2	2.9		
	$^3P^o$	6	7.2		
	$^3D^o$	10	9.1	—	1.3
4P	$^3S^o$	4	3.1		
	$^3P^o$	12	10.3		
	$^3D^o$	20	16.0	—	1.1
2D	$^3P^o$	—	0.1		
	$^3D^o$	—	1.8	—	0.9
	$^3F^o$			—	2.1
2F	$^3D^o$	—	1.7	10	12.8
	$^3F^o$			14	18.3
	$^3G^o$			18	22.0
4F	$^3D^o$	—	1.4	20	13.9
	$^3F^o$			28	21.5
	$^3G^o$			36	25.2
2G	$^3F^o$			—	0.1
	$^3G^o$			—	6.8
	$^3H^o$				
		3×18		7×18	

TABLE XIIb. Calculated multiplet strengths, d^2sp-d^3s (triplets).

d^2s	d^3p	2P		4P		3D		3D		2F		4F		3G		3H	
		1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2
3S	$^3P^o$	—	1	—	2	72.000	67	—	1								
3P	$^3S^o$	2.333	10	42.667	26												
	$^3P^o$	1.750	6	32.000	23	3.375	13	7.875	22								
	$^3D^o$	0.117	4	2.133	9	1.125	6	2.625	15	16.800	42	67.200	45				
4P	$^3S^o$	18.667	11	5.333	22												
	$^3P^o$	14.000	11	4.000	11	27.000	21	63.000	48								
	$^3D^o$	0.933	3	0.267	2	9.000	9	21.000	16	134.400	95	8.400	24				
3D	$^3P^o$	60.750	59	—	0	7.875	9	30.375	30								
	$^3D^o$	20.250	17	—	5	13.125	12	50.625	43	36.000	39	—	10	115.714	99		
	$^3F^o$					1.500	3	5.786	6	18.000	17	—	25				
2F	$^3D^o$	4.800	18	67.200	35	7.000	27	3.000	14	1.200	14	76.800	43				
	$^3F^o$					3.500	13	1.500	6	2.625	12	168.000	94	16.875	72		
	$^3G^o$									0.375	3	24.000	18	10.125	31	33.000	98
4F	$^3D^o$	38.400	22	8.400	27	56.000	32	24.000	14	9.600	8	9.600	40				
	$^3F^o$					28.000	18	12.000	8	21.000	14	21.000	70	135.000	93		
	$^3G^o$									3.000	14	3.000	5	81.000	72	264.000	213
2G	$^3F^o$					40.500	40	48.214	47	84.375	83	—	0	32.411	36		
	$^3G^o$									50.625	37	—	4	81.675	70	178.200	164
	$^3H^o$											—		13.200	13	118.800	119
		3×54		3×54		5×54		5×54		7×54		7×54		9×54		11×54	

a subscript 1, 2, or 3, which indicates the configurations of the parent ion, $3d^24s$, $3d^3$, and $3d4s^2$, respectively. In all those cases where Russell's assignment and the proposed assignment are identical, the limit is written in the middle between the observed and the calculated term.

As an example, we see from Fig. 3 that the two $^3P^o$ terms based on 4P of d^3 and d^2s , respectively, have to be interchanged in their configuration assignment. Although the calculated terms do not fit very accurately, this identification seems fairly certain. Similarly, the two $^3S^o$ terms of d^2sp have to be interchanged in their assignment of the parent terms 2P and 4P , respectively. The same is true for the two $^3S^o$ terms of d^3p . Here the calculated terms alone permit a unique assignment. When we now look for these terms in the tables of multiplet strength, we find these assignments completely confirmed (see especially the super-multiplet $d^2s(^4P)p^3SPD^o-d^2s^2^3P$, Tables VII and XIIa). In many cases the assignment is not so obvious as in the examples given above, but finally only a few doubtful assignments remain. After long and careful consideration the assignments indicated in Figs. 1-3 were adopted. It should be noted that the off-diagonal matrix elements of the configurations d^2sp and d^3p (see reference 6) are sometimes so large that a unique assignment of limits becomes

rather meaningless. This is the case in most of the multiply-occurring terms based on 2P and 4P , or 2F and 4F , respectively. If the line strength tables give no indication for the identification of these terms with one or the other limit, we assign them so as to conform with Russell's classification as closely as possible. In the following we give some of the important points in which the proposed assignment differs from the current one. The details are seen from the figures and tables.

The current assignment of the quintet system is completely confirmed. Both energy terms and multiplet strengths are in satisfactory agreement (Fig. 1 and Tables V, VIII, and IX).

In the singlet system the most important

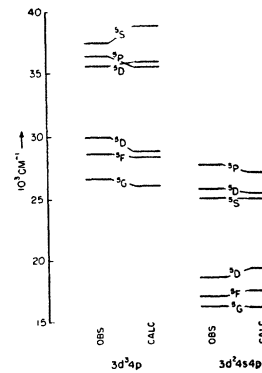


FIG. 1. The deep odd quintet terms of Ti I.

TABLE XIII. Calculated multiplet strengths, d^3p-d^3s (triplets).

d^3	d^3 d^3s	2P		4P		2D		3D		2F		4F		2G		2H	
		1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2
2P	$^3S^{\circ}$	3	2.5	—	0.5	—	—	—	—	—	—	—	—	—	—	—	—
	$^3P^{\circ}$	9	6.0	—	0.0	—	1.0	—	1.9	—	—	—	—	—	—	—	—
	$^3D^{\circ}$	15	9.9	—	4.0	—	0.0	—	0.1	—	0.1	—	1.0	—	—	—	—
4P	$^3S^{\circ}$	—	0.5	3	2.5	—	—	—	—	—	—	—	—	—	—	—	—
	$^3P^{\circ}$	—	0.5	9	7.9	—	0.1	—	0.6	—	—	—	—	—	—	—	—
	$^3D^{\circ}$	—	4.1	15	8.9	—	0.0	—	1.4	—	0.1	—	0.3	—	—	—	—
2D	$^3P^{\circ}$	—	0.1	—	0.0	9	7.0	—	1.9	—	—	—	—	—	—	—	—
	$^3D^{\circ}$	—	0.0	—	0.1	15	12.5	—	2.3	—	0.0	—	0.0	—	—	—	—
	$^3F^{\circ}$	—	—	—	—	21	15.8	—	4.7	—	0.4	—	0.0	—	0.1	—	—
2D	$^3P^{\circ}$	—	2.4	—	1.1	—	0.9	9	4.6	—	—	—	—	—	—	—	—
	$^3D^{\circ}$	—	0.6	—	0.8	—	2.3	15	10.7	—	0.6	—	0.0	—	—	—	—
	$^3F^{\circ}$	—	—	—	—	—	3.3	21	13.5	—	0.1	—	0.7	—	3.4	—	—
2F	$^3D^{\circ}$	—	0.1	—	0.1	—	0.2	—	0.5	15	14.2	—	0.0	—	—	—	—
	$^3F^{\circ}$	—	—	—	—	—	0.4	—	0.0	21	20.3	—	0.1	—	0.2	—	—
	$^3G^{\circ}$	—	—	—	—	—	—	—	—	27	25.6	—	0.0	—	0.1	—	1.4
4F	$^3D^{\circ}$	—	0.3	—	1.1	—	0.0	—	0.0	—	0.0	15	13.7	—	—	—	—
	$^3F^{\circ}$	—	—	—	—	—	0.2	—	0.8	—	0.1	21	19.9	—	0.0	—	—
	$^3G^{\circ}$	—	—	—	—	—	—	—	—	—	0.1	27	24.1	—	2.5	—	0.3
2G	$^3F^{\circ}$	—	—	—	—	—	1.3	—	2.0	—	0.1	—	0.3	21	17.3	—	—
	$^3G^{\circ}$	—	—	—	—	—	—	—	—	—	0.1	—	2.7	27	23.9	—	0.2
	$^3H^{\circ}$	—	—	—	—	—	—	—	—	—	—	—	—	33	27.1	—	5.9
2H	$^3G^{\circ}$	—	—	—	—	—	—	—	—	—	1.2	—	0.2	—	0.5	27	25.1
	$^3H^{\circ}$	—	—	—	—	—	—	—	—	—	—	—	—	—	5.9	33	27.1
	$^3I^{\circ}$	—	—	—	—	—	—	—	—	—	—	—	—	—	—	39	39.0
		3×9		3×9		5×9		5×9		7×9		7×9		9×9		11×9	

change seems to be the reassignment of the w^1P° term as $^1D^{\circ}$. The limit assignment, 2P and d^3 , remains unchanged. There is a very weak line (intensity (1)) which seems to be due to a transition to a^1S of d^2s^2 , and which would contradict this assignment; but this line is not listed

in the new tables,¹³ and the a^1S term is probably spurious.⁴

At this point one should remark on the huge multiplet strength (859) observed for the transition $a^1P-w^1P^{\circ}$, in the notation of the current assignment (Table VI). Theoretically, this line

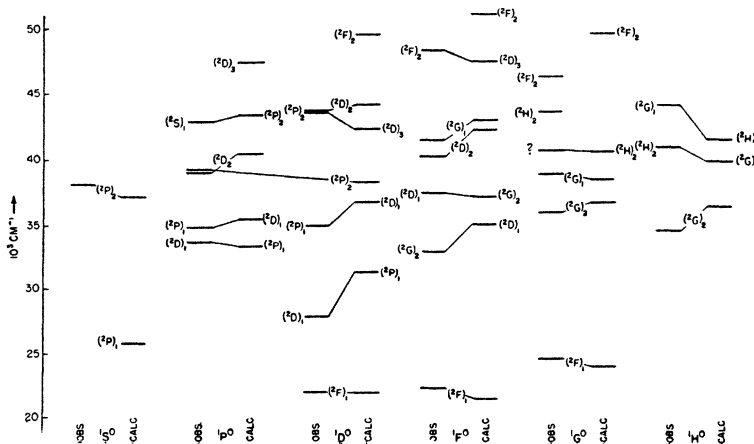
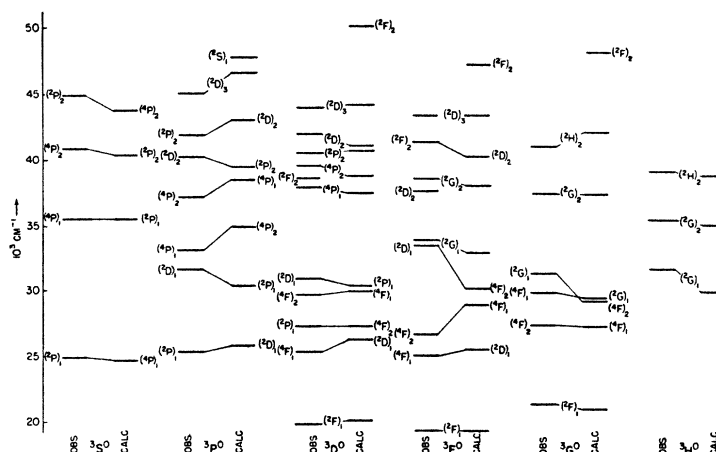


FIG. 2. The deep odd singlet terms of Ti I. The $^1I^{\circ}$ term and the calculated terms above the ionization limit ($55,138 \text{ cm}^{-1}$) are omitted to save space.

FIG. 3. The deep odd triplet terms of Ti I. The $^3I^{\circ}$ term and the calculated terms above the ionization limit (55,138 cm^{-1}) are omitted to save space.



should be weak, in agreement with the measured intensity of 5. Closer inspection shows that this line overlaps with a very strong line of Cr I and is no doubt mainly due to the presence of a small amount of this element.* One cannot exclude the possibility, therefore, that other abnormally strong lines which do not compare with theory might be caused by similar experimental errors.

The assignments of z and y^1P° are somewhat doubtful and may have to be interchanged restoring the original assignment. The prediction of the $^1S^{\circ}$ term of $3d^2 4s 4p$ seems to be of interest.

In both the singlet and the triplet system, the terms based on 2F of d^3 are calculated to lie much higher than was assumed by Russell, and have not been found experimentally, as far as is known to the writer. The inclusion of these terms in the traces for the calculation of the parameters of Table I, columns 1-3, seems to have been the main reason for the large discrepancies.

For the triplet system some reassignments were discussed above. In addition to this, one should note the interchange of the 2P and 2D limits of the $^3P^{\circ}$ and $^3D^{\circ}$ terms, and especially the reassignment of all the terms based on 4F of d^3 and d^2s . The latter assignment seems somewhat doubtful in view of the bad fit of some of the terms and multiplet strengths with 4F limits. A check from an other source seems, therefore, desirable. It is found in the lines connecting related terms in the Fe group. Such lines were first given by Russell.¹⁷ He showed that one

* I am indebted to Prof. D. H. Menzel for pointing this out.

¹⁷ H. N. Russell, *Astrophys. J.* 66, 184 (1927).

obtains smooth curves if one plots the differences between the lowest terms of $d^{n-2}sp$ and $d^{n-2}s^2$, and $d^{n-1}p$ and $d^{n-1}s$, respectively, against n . This is done in Fig. 4, which is taken from Russell's paper with the substitution of the new assignment for Ti I. Russell's assignment is also indicated. The new assignment is seen to give smoother curves. In addition, these curves indicate that some of the lowest terms of the configurations d^4p and d^3sp of VI have wrong assignments.

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My thanks are due first of all to Professor Henry Norris Russell for two very interesting and stimulating discussions. I would also like to thank Professor J. H. Van Vleck for helpful suggestions, and Professor G. Racah of the Hebrew University in Jerusalem for his continued interest in this work. Finally, I wish to thank Professor

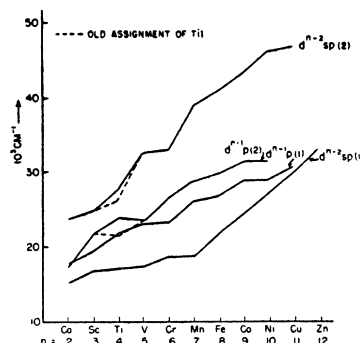


FIG. 4. Related terms in the iron group. The lowest terms of $d^{n-2}sp$ and $d^{n-1}p$ are drawn relative to the lowest terms of $d^{n-2}s^2$ and $d^{n-1}s$, respectively.

E. B. Wilson for permission to use his electric network for secular equations, and Mr. R. H. Hughes for assistance in the work on it.

APPENDIX

Multiplet Strengths for Transitions Involving Equivalent Electrons

Let $\Psi(l^n JM)$ be the normalized anti-symmetric wave function of the configuration given in the brackets. The complete set of quantum numbers is indicated by a typical angular momentum characterized by J and M . We write

$$\psi(l^{n-1}(J')lJM) \sum_{mM'} \Psi(l^{n-1}J'M') \times \Psi(ljm)(J'jM'm|J'jJM),$$

$$\Psi(l^n JM) = \sum_{J'} \psi(l^{n-1}(J')lJM)(l^{n-1}(J')lJ||l^n J).$$

Here ψ is anti-symmetric only in the group of equivalent electrons.

The above equations define $\Psi(l^n)$ in terms of $\Psi(l^{n-1})$ and the coefficients of fractional parentage $(l^{n-1}l||l^n)$. Tables of these coefficients for p^n and d^n were given by Racah.¹⁶

Consider now the transition $l^{n-1}l' \cdot l'' - l^n \cdot l'$. In order to express its multiplet strengths in terms of the multiplet strengths of the transition $l^{n-1}l' \cdot l'' - l^{n-1}l' \cdot l$ which can be calculated by means of Kronig's formulae,¹⁴ we need the unitary transformation¹⁶

$$(l^{n-1}(J_1) \cdot l'J | l^{n-1}l'(J_2) \cdot lJ) = [(2J_1+1)(2J_2+1)]^{\frac{1}{2}} W(J_1 j' j J_2; J J').$$

This transformation changes the order in which the last two electrons are coupled to the rest. The dot separates the groups of electrons which are coupled last. The letters $j, j',$ and J' denote the typical angular momenta of $l, l',$ and l^{n-1} . The function W is defined as follows:¹⁸

$$W(abcd; ef) = \left[\frac{(a+b-e)!(b+e-a)!(e+a-b)!(c+d-e)!(d+e-c)!(e+c-d)!(a+c-f)!}{\times (c+f-a)!(f+a-c)!(b+d-f)!(d+f-b)!(f+b-c)!} \right]^{\frac{1}{2}}$$

$$\times \frac{(a+b+e+1)!(c+d+e+1)!(a+c+f+1)!(b+d+f+1)!}{(a+b+c+d+1-z)!} \times \sum_z (-1)^z \frac{z!(e+f-a-d+z)!(e+f-b-c+z)!}{(a+b-e-z)!(c+d-e-z)!(a+c-f-z)!(b+d-f-z)!}$$

Combining this transformation with the coefficient of fractional parentage we obtain

$$\Psi(l^n(J_1) \cdot l'JM) = (n+1)^{-\frac{1}{2}} \sum_P (-1)^P \Psi(l^n(J_1) \cdot l_p'JM)$$

$$= (n+1)^{-\frac{1}{2}} \sum_P (-1)^{P+1} \sum_{J_2} \psi(l^{n-1}l_p'(J_2) \cdot lJM) \times (l^{n-1}l'(J_2) \cdot lJ || l^n(J_1) \cdot l'J),$$

$$(l^n l'(J_2) \cdot lJ || l^n(J_1) \cdot l'J) = \sum_{J'} (l^{n-1}l'(J_2) \cdot lJ | l^{n-1}l(J_1) \cdot l'J) \times (l^{n-1}(J')lJ_1 || l^n J_1).$$

TABLE XIV. $3(d^2s(S_2L_2) \cdot d2L || d^2(S_1L_1) \cdot s2L)^2$.

$\begin{matrix} d^2s \\ d^3 \\ d^2s \end{matrix}$	$\begin{matrix} sP \\ 4P \end{matrix}$	$\begin{matrix} sF \\ 4F \end{matrix}$
$\begin{matrix} 4P \\ 4F \end{matrix}$	$\begin{matrix} 8/5 \\ 7/5 \end{matrix}$	$\begin{matrix} 3/5 \\ 12/5 \end{matrix}$

The groups l^n and $l^{n-1}l$ consist of the electrons $1, 2 \dots p-1, p+1, \dots n+1,$ and P is the parity which exchanges p with $n+1$.

A typical matrix element of the electric dipole moment,

$$P = \sum_{i=1}^{n+1} p_i,$$

is therefore

$$\int \Psi^*(l^{n-1}l'(J_2) \cdot l''J'') P \Psi(l^n(J_1) \cdot l'J) d\tau = (n+1) \int \Psi^*(l^{n-1}l'(J_2) \cdot l''J'') p_i \times \Psi(l^n(J_1) \cdot l'J) d\tau$$

$$= n^{-\frac{1}{2}} \sum_{P, Q, R} (-1)^{P+Q+R+1} \sum_{J_2'} \int \Psi^*(l^{n-1}l'_q) \times (J_2, l_r'' J'') p_i \psi(l^{n-1}l'_p(J_2') \cdot lJ) d\tau \cdot (l^{n-1}l'(J_2')lJ || l^n(J_1)l'J).$$

¹⁸ G. Racah, Phys. Rev. 62, 438 (1942).

TABLE XV. $3(d^2s(S_2L_2) \cdot d0L) [d^3(S_1L_1) \cdot s0L]^2$.

$\begin{matrix} d^2s \\ d^3s \end{matrix}$	1P 2P	1D 3D	1D 3D	1F 2F	1G 3G	1H 3H
2S		4/5				
2P	7/10	9/20	21/20	6/5		
2D	3/2	1/4	27/28	3/7	5/7	
2F	4/5	21/20	9/20	3/10	3/2	3/2
2G		9/20	15/28	15/14	11/14	3/2

TABLE XVI. $3(d^2s(S_2L_2) \cdot d1L) [d^3(S_1L_1) \cdot s1L]^2$.

$\begin{matrix} d^2s \\ d^3s \end{matrix}$	3P 2P	3P 4P	3D 3D	3D 3D	3F 2F	3F 4F	3G 2G	3H 2H
2S			4/5					
2P	7/90	64/45	1/20	7/60	2/15	8/15		
4P	28/45	8/45	2/5	14/15	16/15	1/15		
2D	3/2		1/4	27/28	3/7		5/7	
2F	4/45	56/45	7/60	1/20	1/30	32/15	1/6	1/6
4F	32/45	7/45	14/15	2/5	4/15	4/15	4/3	4/3
2G			9/20	15/28	15/14		11/14	3/2

The wave function ψ^* is anti-symmetrical in the group l^{n-1} consisting of the electrons $1, 2, \dots, q-1, q+1, \dots, r-1, r+1, \dots, n+1$. The parities of the permutations which exchange q with n , and r with $n+1$ are denoted by Q and R , respectively. The matrix element vanishes unless the two configurations differ by one electron only, and unless all corresponding electrons have the same parity. It follows, therefore, that

$$P = Q + 1, \quad J_2' = J_2, \quad i = r = n + 1.$$

Since there are n ways of realizing this, we obtain

$$\begin{aligned} & (l^{n-1}l'(J_2) \cdot l''J'' | \mathbf{P} | l^n(J_1) \cdot l'J) \\ &= n \int (l^{n-1}l'(J_2) \cdot l_{n+1}''J'' | \mathbf{p}_{n+1} | l^{n-1}l'(J_2) \cdot l_{n+1}J) \\ & \quad \times (l^{n-1}l'(J_2)lJ | l^n(J_1)l'J). \end{aligned}$$

The multiplet strength now becomes

$$\begin{aligned} & S(l^{n-1}l'(J_2) \cdot l''J''; l^n(J_1) \cdot l'J) \\ &= nS(l^{n-1}l'(J_2) \cdot l''J''; l^{n-1}l'(J_2) \cdot lJ) \\ & \quad \times (l^{n-1}l'(J_2) \cdot lJ | l^n(J_1) \cdot l'J)^2. \end{aligned}$$

The multiplet strength on the right hand side is for a transition which does not involve an equivalent electron, and can be calculated, therefore, from Kronig's formulae. The transition $l^{n-1}l' \cdot l'' - l^n \cdot l'$ occurs in the Fe group as $d^{n-1}sp - d^n s$.

Similarly, one finds easily for the transition array $l^n - l^{n-1} \cdot l'$

$$\begin{aligned} & S(l^n J'(J_1); l^{n-1}(J_1)l'J) \\ &= nS(l^{n-1}(J_1)lJ'; l^{n-1}(J_1)l'J) (l^{n-1}(J_1)lJ' | l^n J')^2, \end{aligned}$$

and for $l^n l' \cdot l'' - l^n \cdot l'^2$

$$\begin{aligned} & S(l^n l'(J_1) \cdot l''J'; l^n(J_1') \cdot l'^2(J_2)J) \\ &= 2S(l^n l'(J_1) \cdot l''J'; l^n l'(J_1) \cdot l'J) \\ & \quad \times (l^n l'(J_1) \cdot l'J | l^n(J_1') \cdot l'^2(J_2)J)^2. \end{aligned}$$

The unitary transformation occurring in the last equation can again be expressed in terms of the function W ; one obtains¹⁶

$$\begin{aligned} & (j_1 j_2(J') \cdot j_3 J | j_1 \cdot j_2 j_3(J'')J) \\ &= [(2J' + 1)(2J'' + 1)]^{\frac{1}{2}} W(j_1 j_2 J j_3; J' J''). \end{aligned}$$

From these formulae one can readily calculate the multiplet strengths of the transition arrays $d^n - d^{n-1}p$ and $d^n sp - d^n s^2$ occurring in the Fe group.

It is convenient to measure the absolute multiplet strength in units of the square of the radial integral over the electric dipole moment

$$\sigma = -|e| [(2l+1)(2l'+1)]^{-\frac{1}{2}} \int_0^\infty r R(nl)R(n'l')dr$$

where $R(nl)$ and $R(n'l')$ are r times the normalized radial parts of the one-electron wave functions of the initial and final state of the jumping electron. Since these functions differ for different configurations, the values of S are not comparable between different transition arrays. With this normalization

$$\begin{aligned} & \sum_{S_2 L_2 L''} S(l^{n-1}l'(S_2 L_2) \cdot l'' S L''; l^n(S_1 L_1) \cdot l' S L) \\ &= (n/2)(2S+1)(2L+1)(l+l'+1)(2l''+1). \end{aligned}$$

These sums are indicated in Tables VIII–XIII.

As a numerical example we may calculate the array $d^2 sp - d^3 s$ of Ti *I*. The parentage coefficients of multiplet strength $3(d^2 s(S_2 L_2) \cdot dSL) [d^3(S_1 L_1) \cdot sSL]^2$, which result from the above equations that are listed in Tables XIV–XVI for the quintet, singlet, and triplet system, respectively. They agree with those calculated by Menzel and Goldberg.¹⁹ However, these authors

¹⁹ D. H. Menzel and L. Goldberg, *Astrophys. J.* **84**, 1 (1936)

were not able to separate the parentages of multiply occurring terms. The formulae derived above overcome this difficulty.

Kronig strengths for a great number of transitions were calculated by Goldberg.²⁰ His tables have to be multiplied by suitable factors to comply with the normalization adopted above.²¹ From the Kronig strengths for $d^2s \cdot p - d^2s \cdot d$ and

²⁰ L. Goldberg, *Astrophys. J.* **82**, 1 (1935).

²¹ L. Goldberg, *Astrophys. J.* **84**, 11 (1936).

the parentages of Tables XIV–XVI we then obtain the multiplet strengths for $d^2s \cdot p - d^3 \cdot s$ as listed in Tables VIII, X, and XII, column 1. When these values are summed over the multiply-occurring terms of both configurations one obtains the multiplet strengths listed by Goldberg.²⁰

In the same fashion other tables of multiplet strength relevant to Ti *I* are calculated and are given in Tables IX–XIII, column 1.

The Zeeman Effect in Microwave Molecular Spectra*

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A microwave cavity spectroscope is described, which possesses a high sensitivity and resolution for the observation of the Zeeman effect of molecular absorption lines in the microwave frequency range. The theory of operation for this spectroscope and the criteria for sensitivity are formulated.

The Zeeman effect of a number of microwave spectral lines has been measured for the gas molecules $N^{14}H_3$, $N^{15}H_3$, and CH_3Cl^{35} and observed for CH_3Cl^{37} and SO_2 . All the experimental results obtained so far can be satisfactorily explained by the combined magnetic contribution due to nuclear and molecular *g* factors, if there exists a spin-rotation coupling, or solely by the magnetic contribution due to molecular rotation, if there is no such coupling. Thus, further knowledge of the nuclear and molecular magnetic properties of molecules can be obtained through the examination of the Zeeman effect in microwave absorption spectra.

I. INTRODUCTION

THROUGHOUT the history of atomic spectra, the study of the Zeeman effect has provided an exceedingly powerful tool in elucidating the mechanism of the emission and absorption of radiation energy. It gave a great impetus to the early electron theory by emphasizing the important role of the electron in the radiation process. It laid a physical basis for the theory of space quantization, which is an important feature of the quantum theory. Then, the unassailable evidence of the "anomalous" Zeeman effect which had puzzled physicists for a quarter of a century finally led, together with the phenomenon of multiplet structure, to the

introduction of the electron spin hypothesis. It soon became clear that an analogous situation existed in the atomic hyperfine structure, where the nuclear spin played a role similar to that of the electron spin in the atomic fine structure. The Zeeman effect became again instrumental in clarifying the situation through the effect of the magnetic moment, associated with the nuclear spin, in an external magnetic field.

The advent of microwave techniques in recent years has given rise to a new branch of spectroscopy. It has been found that a microwave system used as a spectroscopic instrument is capable of a very high resolving power, essentially because the frequency is directly measurable. Such a property can be used to great advantage for investigating the Zeeman effect, since measurements are possible with hyperfine line splittings in a fairly weak magnetic field,

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