On the Deep Configurations of Ti I, Ti II, V II, V III

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The theoretical formulas for d^ns^2, $d^{n+1}s$, d^{n+2} are compared with the experimental data of Ti II, V III, Ti I, V II. In Ti II and V II the agreement is considerably improved by taking into account the interactions between configurations.

INTRODUCTION

It is a known fact[1] that in the iron group the configurations $3d^n4s^2$, $3d^{n+1}4s$, $3d^{n+2}$ overlap considerably. As they are all even, their proximity gives rise to strong interactions and we must, therefore, expect a mixing up of the terms and large deviations from the first-order formulas. Consequently the iron group is most suitable for investigating configuration interactions when we confine ourselves to (LS) coupling. On the one hand, in the elements of the preceding periods the distance between configurations of the same parity is comparatively great, so that the interactions are small, and on the other hand, in the succeeding periods the (LS) coupling is increasingly broken down.

As the only detailed studies of these configurations in the iron group are those which have been made by Ufford[2] and Marvin,[3] and as these studies were since made more theoretical although experimental data have been obtained, it has been thought worth while to consider systematically the spectra arising from these configurations. We confined ourselves however to four spectra as they alone afford sufficient data for detailed study.

In each of the spectra which was studied we fitted the experimental values to the theoretical formulas first by neglecting configuration interactions (first-order comparison), and then, when the overlapping of the configurations was considerable, we took those interactions into account. In both cases we evaluated the Slater-Condon F's and G's by the method of least squares, calculated the terms and compared the agreements in the two cases.

Following Ufford[2] we worked on the assumption that the radial integrals containing electrons of identical n and l values are equal, regardless of the fact that these electrons belong to different configurations. The question whether it is justifiable to do so will be discussed in detail in the case of V II, as in that case there could have been some doubts as to the soundness of the assumption.

The experimental data were mainly taken from the tables of Bacher and Goudsmit.[4] In V II we used the classification of Meggers and Moore[5] as it is given by Bowman,[6] because the original paper was unfortunately not at our disposal.

The theoretical formulas are taken from Racah.[7]

Ti II

In the three configurations ds^2, d^2s, d^3, 15 of the 16 terms predicted by theory are known. This spectrum was considered by Ufford,[2] but it will be shown that a better agreement with the experimental data may be obtained by a fuller use of the least squares, and also by a change in the assignments of a couple of terms.

In the first-order comparison we fitted the experimental values to the theoretical formulas by means of least squares and calculated the mean error μ and mean deviation Δ which are defined by

$$\mu^2 = \Sigma\Delta_i^2/n - m, \quad \Delta^2 = \Sigma\Delta_i^2/n,$$

where Δ_i is the deviation of each term, n the number of terms, and m the number of adjust-

[1] E. U. Condon and G. H. Shortley, *Theory of Atomic Spectra* (Cambridge University Press, New York, 1935), p. 330.
[2] C. W. Ufford, Phys. Rev. **44**, 732 (1933).
[3] H. H. Marvin, Phys. Rev. **47**, 521 (1935).
[4] R. F. Bacher and S. Goudsmit, *Atomic Energy States* (McGraw-Hill Book Company, Inc., New York, 1932).
[5] W. F. Meggers and C. E. Moore, J. Research Nat. Bur. Stand. **25**, 83 (1940).
[6] D. S. Bowman, Phys. Rev. **59**, 386 (1941).
[7] G. Racah, Phys. Rev. **62**, 438 (1942); **63**, 367 (1943).

TABLE I. Calculated terms of the deep configurations of Ti II.

Column (1). Neglecting configuration interactions, using old assignments. Column (2). Neglecting configuration interactions, using proposed assignments. Column (3). With configuration interactions, using old assignments. Column (4). With configuration interactions, using proposed assignments.

Term	Obs.	(1) Calc.	(1) Diff.	(2) Calc.	(2) Diff.	(3) Calc.	(3) Diff.	(4) Calc.	(4) Diff.
$a\ ^4F$	225	454	+229	−146	−371	898	+673	214	−11
$b\ ^4F$	1085	123	−962	701	−384	515	−570	1160	+75
$d^2s\ ^2F$	4783	5928	+1145	5832	+1049	5153	+370	5079	+296
$d^2s\ ^2D$	8730	9373	+643	9630	+900	8711	−19	8947	+217
$d^3\ ^2G$	9065	8489	−576	8402	−663	8837	−228	8749	−316
$d^3\ ^4P$	9452	9872	+420	9621	+169	9572	+120	9310	−142
$d^3\ ^2P$	9934	11739	+1805	11658	+1724	10020	+86	9932	−2
$d^2s\ ^4P$	9968	10203	+235	10468	+500	9955	−13	10256	+288
$d^3\ ^2D^-$	12706	12441	−265	12413	−293	13651	+945	13637	+931
$d^3\ ^2H$	12730	11739	−991	11658	−1072	12163	−567	12055	−675
$d^2s\ ^2G$	15261	13922	−1339	14187	−1074	14066	−1195	14328	−933
$d^2s\ ^2P$	16589	15676	−913	15598	−991	16519	−70	16464	−125
$d^3\ ^2F$	20918	21487	+569	21424	+506	21386	+468	21317	+399
$d^2s\ ^2S$	21338	30031	(+8693)*	30605	(+9267)*	30154	(+8816)*	30757	(+9419)*
$ds^2\ ^2D$	25100	25100	0	25100	0	25100	0	25100	0
$d^3\ ^2D^+$	—	33022	—	33152	—	33625	—	33674	—
Mean error			±1147		±1090		±742		±622
Mean deviation			± 867		± 824		±525		±440

Parameters:	(1)	(2)	(3)	(4)
$A(d^2s)$	9303	9330	8676	8735
$A(d^3)$	9872	9621	9572	9310
$A(ds^2)$	25100	25100	25656	25587
$B=F_2-5F_4$	650	651	604	606
$C=35F_4$	1922	1981	2071	2128
G_2	1824	1710	1474	1362
$H_2=R^2(dd, ds)/35$	—	—	172	172

* This term has not been taken into account in the least squares calculations.

able parameters. In all the calculations we excluded $d^2s\ ^2S$ as it fits badly[8] in most spectra arising from d^2s. The results of the calculation are shown in Table I, column (1).

It must be remembered that, according to theory, the two quartets F should be in the same order and at the same distance as the quartets P, while in the given classification the order is inverted. The question arises whether the assignments of one pair of quartets should be interchanged, and, if so, of which of the two pairs. We examined all possibilities and found that the best agreement is obtained by interchanging the assignments of the quartets F, i.e., by assigning $_a{}^4F$ to d^3 and $_b{}^4F$ to d^2s.

With this exchange we repeated the last calculation and obtained the results shown in Table I, column (2). We must admit that the agreement in column (2) has not been appreciably improved, but it will be shown that the interaction calculations will justify the exchange in assignments.

We proceeded to the second step in the comparison by taking the configuration interactions into account. As most of the formulas obtained by introducing interactions are not linear, we used the usual approximate method of least squares.[9] As the approximate values of the parameters we took the results of the first-order comparison, and the approximate value of the interaction parameter H_2 was roughly evaluated by its effect on the position of the doublets PFG. The derivatives needed in Eq. (13-93) of Margenau[9] were obtained by the explicit formulas in the case of the second-order equations. In the case of the fourth-order equation they were obtained by the following method. We inserted in the matrix the approximate parameters and evaluated the roots of the secular equation. From these roots we found the orthogonal transformation which diagonalizes the numerical matrix and applied that transformation to the original matrix (in terms of the parameters). It is easy to show that the coeffi-

[8] Reference 1, p. 204.

[9] H. Margenau and G. M. Murphy, *The Mathematics of Physics and Chemistry* (Van Nostrand Company, New York, 1943), p. 500.

cients of the different parameters in the diagonal elements of the transformed matrix are the values of the required derivatives.

By the use of these methods the theoretical formulas became linear formulas containing as adjustable constants the correction terms of the parameters. We made two calculations. In the first calculation we used the old assignments and in the second we used the exchanged assignments of the quartets F. The results are shown in Table I, columns (3) and (4). The agreement of the quartets F in the proposed assignments is now much better than in the old assignments. It will be observed that the agreement of the remaining terms is practically the same in the two calculations, the mean deviation, excluding the quartets F, being ± 506 and ± 475. This shows the advantage of using least squares in comparing the theoretical formulas with experimental data; an incorrect assignment in the classification when many terms are known does not appreciably change the values of the parameters, as its effect is mainly balanced by the other terms.

To sum up, the agreement with experimental data has been greatly improved by taking configuration interactions into account; the mean error has been reduced from ± 1090 to ± 622. It is interesting to note that even the agreement of the unperturbed terms (the quartets F and P, and ^2H) is improved.

Finally we shall compare our results with those of Ufford. Using the parameters evaluated by him, one obtains a mean deviation of ± 859 cm^{-1}. By the full use of the method of least squares, the mean deviation is reduced to ± 525 when the same assignments of the quartets F are retained and to ± 440 when the assignments are exchanged as proposed above.

TABLE II. The deep configurations of V III.

Term	Obs.	Calc.	Diff.
$d^3\ {}^4F$	336	387	+51
$d^3\ {}^4P$	11668	11873	+205
$d^3\ {}^2G$	12089	12015	−74
$d^3\ {}^2D^-$	16317	17197	+880
$d^3\ {}^2H$	16907	15844	−1063
$d^3\ {}^2P$	—	15844	—
$d^3\ {}^2F$	—	27329	—
$d^3\ {}^2D^+$	—	42756	—
$d^2s\ {}^4F$	44343	44343	0
$d^2s\ {}^2F$	49602	49602	0
$d^2s\ {}^4P$	—	55829	—
$d^2s\ {}^2D$	—	55634	—
$d^2s\ {}^2G$	—	60994	—
$d^2s\ {}^2P$	—	61087	—
$d^2s\ {}^2S$	—	82926	—
Mean error			±989

Parameters: $A(d^3)=11873$, $A(d^2s)=53975$, $B=F_2-5F_4=766$, $C=35F_4=2855$, $G_2=1753$.

V III

In the deep configurations, 8 terms have been classified by White.[10] It must be pointed out that, according to theory, $d^3\ {}^2H$ and $d^3\ {}^2P$ should be, in the first approximation, at the same height, while in White's classification ^2P lies at about 5600 cm^{-1} lower than ^2H and is even lower than $d^3\ {}^4P$. This cannot be ascribed to a repulsion from $d^2s\ {}^2P$, as the configuration d^2s is so high that the interactions between it and d^3 must be much smaller than the corresponding interactions in Ti II, and in the latter ^2P is shifted by only 1700 cm^{-1}. Moreover, White's classification of $d^3\ {}^2P$ is based on the only multiplet $3d^3\ {}^2P-3d^2({}^3F)4p\,{}^2D^0$, or more exactly on the only line $\lambda=1289$A which is assigned to the transition ${}^2P_{3/2}-{}^2D_{5/2}{}^0$, the existence of the other two lines of this multiplet being only inferred by assuming that they coincide by

TABLE III. The deep configurations of Ti I.

Term	Obs.	Calc.	Diff.
$d^2s^2\ {}^3F$	223	712	+489
$d^3s\ {}^5F$	6721	6020	−701
$d^2s^2\ {}^1D$	7255	7194	−61
$d^2s^2\ {}^3P$	8547	9119	+572
$d^3({}^4F)s\ {}^3F$	11673	11182	−491
$d^2s^2\ {}^1G$	12118	11118	−1000
$d^3s\ {}^5P$	14055	14427	+372
$d^2s^2\ {}^1S$	15167	25916	(+10749)*
$d^3s\ {}^3G$	15170	15072	−98
$d^3s\ {}^3D^-$	17467	18660	+1193
$d^3({}^2P)s\ {}^3P$	18101	17874	−227
$d^3s\ {}^3H$	18133	17874	−259
$d^3s\ {}^1G$	18288	17653	−635
$d^3({}^4P)s\ {}^3P$	18873	19589	+716
$d^3s\ {}^1P$	20063	20456	+393
$d^3s\ {}^1D^-$	20210	21241	+1031
$d^3s\ {}^1H$	20796	20456	−340
$d^3({}^2F)s\ {}^3F$	—	26282	—
$d^3s\ {}^1F$	29818	28863	−955
$d^3s\ {}^3D^+$	—	36779	—
$d^3s\ {}^1D^+$	—	39361	—
Mean error			±772

Parameters: $A(d^2s^2)=5196$, $A(d^3s)=18299$, $B=F_2-5F_4=560$, $C=35F_4=1840$, $G_2=1291$.

* This term has not been taken into account in the least squares calculation.

[10] H. E. White, Phys. Rev. 33, 674 (1929).

TABLE IV. Calculated terms of the deep configurations of V II.

Column (1). Neglecting configuration interactions. Column (2). With configuration interactions. Column (3). Assuming that the parameters B and C differ in the two configurations.

Term	Obs.	(1) Calc.	(1) Diff.	(2) Calc.	(2) Diff.	(3) Calc.	(3) Diff.
d^4 ^5D	206	−1502	−1708	−1136	−1342	427	+221
d^3s ^6F	2926	4810	+1884	4697	+1771	3790	+864
$d^3(^4F)s$ ^3F	8904	10913	+2009	10122	+1218	9893	+989
d^4 $^3P^-$	11709	12286	+577	11940	+231	12656	+947
d^4 ^3H	12634	10857	−1777	11122	−1512	11509	−1125
d^4 $^3F^-$	13558	12715	−843	13423	−135	13160	−398
d^3s ^5P	13647	14694	+1047	14578	+931	13924	+277
d^4 ^3G	14572	14152	−420	14055	−517	14651	+79
d^3s ^3G	16446	16264	−182	16472	+26	16194	−252
d^4 $^1G^-$	17911	18043	+132	17917	+6	17819	−92
d^4 ^3D	18317	18764	+447	18494	+177	19050	+733
d^3s ^1G	19113	19316	+203	19295	+182	19245	+132
$d^3(^2P)s$ ^3P	19147	19559	+412	19447	+300	19572	+425
d^4 ^1I	19191	17037	−2154	17319	−1872	17050	−2141
d^4 $^1S^-$	19902	21321	+1419	21561	+1659	20806	+904
$d^3(^4P)s$ ^3P	20238	20797	+559	20859	+621	20027	−211
d^3s ^3H	20303	19559	−744	19406	−897	19572	−731
d^3s $^3D^-$	20601	20711	+110	21056	+455	20972	+371
d^4 $^1D^-$	20981	22980	+1999	20931	−50	22597	+1616
d^3s ^1P	22274	22610	+336	22328	+54	22623	+349
d^3s ^1H	23391	22610	−781	22328	−1063	22623	−768
d^3s $^1D^-$	25191	23763	−1428	25577	+386	24024	−1167
d^4 ^1F	26840	26920	+80	26400	−440	26476	−364
d^4 $^3F^+$	30302	32106	+1804	32407	+2105	31366	+1064
$d^3(^2F)s$ ^3F	30637	29442	−1195	29313	−1324	29706	−931
d^4 $^3P^+$	32169	32534	+365	33021	+852	31870	−299
d^3s ^1F	34229	32494	−1735	33008	−1221	32757	−1472
d^4 $^1G^+$	36425	36501	+76	36883	+458	35276	−1149
d^3s $^3D^+$	44139	42625	−1514	42401	−1738	43935	−204
d^3s $^1D^+$	44658	45677	+1019	45332	+674	46987	+2329
d^4 $^1D^+$	—	50013	—	50488	—	48093	—
d^4 $^1S^+$	—	65143	—	65347	—	61853	—
Mean error			±1295		±1142		±1083
Mean deviation			±1182		±1021		± 948

Parameters:	(1)	(2)	(3)
$A(d^4)$	12335	12697	13624
$A(d^3s)$	19271	19029	18501
$B=F_2-5F_4$	659	659	d^3s:676, d^4:628
$C=35F_4$	2431	2417	d^3s:2725, d^4:2142
G_2	1526	1484	1526
$H_2=R^2(dd, ds)/35$	—	153	—

chance with two other lines. Consequently we concluded that the levels 11207 cm^{-1} and 11387 cm^{-1} given by White most probably do not exist, and we excluded $d^3\ ^2P$ from the calculation. The results are shown in Table II.

It is not worth while to consider configuration interactions as the configurations are very widely separated.

Ti I

As only one term of the configuration d^4 is known, we considered only d^3s and d^2s^2 in which 18 of the 21 terms predicted by theory are known. Here also $d^2s^2\ ^1S$ fits badly, and we excluded it from the calculations. The results of the first-order comparison are shown in Table III. The agreement is satisfactory—a mean error of ±772 amounts only to 2.5 percent of the configurations' width. This is only to be expected as the configurations d^3s and d^2s^2 overlap very slightly, and d^4 is probably very high. As a result the interactions are small and it is not worth while to consider them.

V II

According to the classification of Meggers and Moore[5] all except two of the terms are known in the configurations d^3s and d^4, but d^2s^2 is altogether unknown. In making a preliminary calculation we got rid of the non-linear formulas by taking means of each two terms of the same kind. The parameters obtained were $A(d^4) = 10741$, $A(d^3s) = 18403$, $B = 581$, $C = 2589$, $G_2 = 1361$, and from them the terms were calculated. It was found that the observed value of the term ^1D (44658) agrees better with the calculated value of $d^3s\ ^1D^+$ (44451) than with that of $d^4\ ^1D^+$ (47699). This suggests that the observed value should be assigned to $d^3s\ ^1D^+$ and not to $d^4\ ^1D^+$, the term to which Meggers and Moore assigned it, and in fact subsequent calculations confirmed this new assignment. Those subsequent calculations also gave rise to doubts as to the correctness of the assignments of the two $d^3s\ ^3P$. In addition the examination of the separations of the two triplets could not give any information, as theoretically those separations are almost equal (they are in the ratio 4:5). Therefore, in some of the calculations made by least squares we used only the mean of the two triplets, and it was found that the agreement was considerably improved by exchanging the assignments of the $d^3s\ ^3P$ terms, i.e., by assigning the observed value 19147 to $d^3(^2P)s\ ^3P$ and the observed value 20238 to $d^3(^4P)s\ ^3P$. Consequently these proposed assignments for $^1D^+$ and ^3P were used in all calculations which are reported in this paper.

The first-order calculation gave the results shown in Table IV, column (1). Introducing interactions between d^3s and d^4 we obtained the results in Table IV, column (2). It will be seen that the introduction of the interactions brings about some improvement of the agreement, although not a very considerable one.

A first-order comparison was made also by Bowman,[6] who assumed that the parameters F_2 and F_4 differ in the two configurations d^3s and d^4. From his results it is found that the parameters B differ by 40 percent and the parameters C differ by 20 percent in the two configurations. According to Ufford[2] and Racah[11] it is difficult to admit such differences. Since Bowman's calculations are based on Ostrofsky's[12] formulas for d^4 in which there are some mistakes, we repeated those calculations. We assumed as Bowman did that the parameters B and C differ in the two configurations, but we used the correct formulas for d^4 and the proposed assignments, and made full use of the least squares. The results are shown in Table IV, column (3). The parameters B then differed by only 7 percent but C differed by 25 percent. We must admit that a better agreement is obtained by assuming different values for B and C than by assuming unified parameters, but the gain in mean error is not great enough to justify such a procedure which has no sufficient theoretical basis.

I am deeply grateful to Professor G. Racah for suggesting this problem and for his constant assistance to me throughout my work.

[11] G. Racah, Phys. Rev. **61**, 537 (1942).
[12] M. Ostrofsky, Phys. Rev. **46**, 604 (1934).