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Low Even Configurations of the First Spectrum of Molybdenum (Mo I)

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The analysis of the first spectrum of molybdenum has been extended by the classification of approximately 3,000 additional lines arising from combinations including 44 new even levels and 190 new odd levels that have been located. The identification of those levels that belong to the three low even configurations, $4d^4\,5s^2$, $4d^5\,5s$, and $4d^6$, is given. Some unpublished levels found earlier by C. C. Kiess are included.

Assignment of the terms to the three low even configurations has been aided by a theoretical calculation. Over-all agreement is very good, as indicated by a mean deviation of ± 168 cm^{-1} between theory and experiment. The calculation is presented in a simplified and detailed form, which may help in applying the theory to future analyses.

The theoretical calculation assumes LS-coupling and takes into account the electrostatic interaction between the three configurations. Excellent confirmation of the theory of configuration interaction is obtained because the interaction is very strong in Mo I. Difficulties in assigning a term to a configuration are discussed and tentatively resolved by the use of the calculation.

In the $3d^5\,4s$ configuration of Fe III, Trees has shown that polarization can be accounted for by an empirical correction proportional to $L(L+1)$. The applicability of this correction in the $4d^5\,5s$ configuration of Mo I is demonstrated. The correction is only about half as important in Mo I as it is in Fe III, so that Mo I is not well suited for a detailed study of polarization effects. However, the agreement obtained is some confirmation of Racah's assumption that polarization can be treated linearly.

Magnetic interactions are considered briefly in an effort to explain disagreements between theory and experiment, and to illustrate additional difficulties that arise in the assignment of term designations.

1. Introduction and Summary of Results

Work on Mo I was started at the National Bureau of Standards more than 30 years ago and has continued intermittently here ever since. Recently, a new description of the spectrum was made from spectrograms obtained over this period with NBS spectrographs. This paper has a two-fold purpose: (1) to report preliminary results for the analysis of the low even configurations from this latest description of Mo I, and (2) to describe the theoretical calculation of the term values of these configurations.

(1) The molybdenum atom has 42 electrons of which the outer six give rise to the first spectrum. These electrons arrange themselves into the three configurations, $4d^4\,5s^2$, $4d^5\,5s$, and $4d^6$ giving rise to low even terms, and into other configurations having higher even and odd terms. Previous work on the analysis of Mo I has been published by Kiess [1],[1] Catalán [2], Meggers and Kiess [3], and Catalán and Madariaga [4]. The last paper contains the most complete published analysis, which consists of 119 quintet and septet levels; it includes the $a\,^7S$ ground state and all the low quintet terms, except $a\,^5F$ and the levels $a\,^5D_0$ and $c\,^5D_1$.

In the present investigation 44 new triplet and singlet levels of the low even configurations have been identified. We are in indebted to C. C. Kiess for permission to use some of his unpublished levels, which include the $a\,^5F$ term and the levels $c\,^5D_1$, $a\,^3D_2$, $a\,^3D_3$, $a\,^3F_2$, $b\,^3D_3$, and $b\,^3F_3$. There are now known 19 levels of 8 terms of the $4d^4\,5s^2$ configuration, 49 levels of 18 terms of the $4d^5\,5s$ configuration, and 9 levels of 3 terms of the $4d^6$ configuration. A complete list of the known levels of these configurations is given in table 1. The successive columns of the table give the configuration, term designation, J-value, level, interval, and observed g-value. In table 1 the levels known prior to the present investigation are starred (*).[2]

(2) Some observed term values in Mo I are more than 2000 cm^{-1} from the positions calculated with the Slater first-order theory [5] from the formulas given by Laporte and Platt [6] for the d^4 (and d^6) configurations and by Catalán and Antunes [7] and by Laporte [8] for the d^5 configuration. A theoretical calculation shows that these deviations can be largely explained by inclusion of the effect of configuration interaction among the three lowest configurations. This calculation also helped in identifying certain levels and in predicting the locations of new terms.

The method of treating the second-order effects of configuration interaction has been outlined by Condon [10]. Calculations of the matrix elements of configuration interaction for configurations with d- and s-electrons have been made by Ufford [11] and by Racah [12]. Several comparisons with experiment have been made in spectra with $3d$ and $4s$ electrons [13 to 16]. Ufford's calculation for Zr II [11] furnishes the only detailed comparison between theory and experiment in spectra with $4d$ and $5s$ electrons; this calculation shows that the effects of configuration interaction are very strong

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[1] Figures in brackets indicate literature references at end of this paper.

[2] Almost 190 new odd levels have been discovered so that the total number of known odd levels is now about 230. The odd levels will be included in a complete description and analysis of Mo I to be published later.

TABLE 1. *Low even terms of* Mo I (*cm*$^{-1}$)

Electron configuration	Term designation	J	Level	Interval	Observed g
$4d^5(^6S)5s$	$a\,^7S$	3	*0. 0		1. 98
$4d^5(^6S)5s$	$a\,^5S$	2	*10768. 2		2. 00
$4d^4\,5s^2$	$a\,^5D$	0	*10965. 9	176. 9	
		1	*11142. 8	311. 6	1. 50
		2	*11454. 4	404. 1	1. 52
		3	*11858. 5	487. 8	1. 49
		4	*12346. 3		1. 48
$4d^5(^4G)5s$	$a\,^5G$	2	*16641. 0	51. 9	0. 32
		3	*16692. 9	54. 8	0. 93
		4	*16747. 7	36. 8	1. 14
		5	*16784. 5	−0. 7	
		6	*16783. 8		
$4d^5(^4P)5s$	$a\,^5P$	3	*18229. 1	−127. 3	1. 63
		2	*18356. 4	−123. 3	1. 79
		1	*18479. 7		2. 45
$4d^5(^4D)5s$	$b\,^5D$	0	*19969. 9	160. 4	
		1	*20130. 3	150. 7	1. 59
		2	*20281. 0	69. 5	1. 54
		3	*20350. 5	−192. 7	1. 49
		4	*20157. 8		1. 49
$4d^4\,5s^2$	$a\,^3P$	0	20607. 5	1636. 9	
		1	22244. 4	631. 6	0. 95
		2	22876. 0		1. 41
$4d^5(^4D)5s$	$a\,^3D$	1	20930. 4	20. 4	1. 04
		2	*20950. 8	667. 8	1. 20
		3	*21618. 6		1. 34
$4d^5(^4G)5s$	$a\,^3G$	3	20947. 9	206. 0	0. 78
		4	21153. 9	189. 3	1. 04
		5	21343. 2		1. 21
$4d^4\,5s^2$	$a\,^3F$	4	23516. 5	−151. 6	1. 12
		3	23668. 1	133. 6	1. 08
		2	*23534. 5		0. 68
$4d^4\,5s^2$	$a\,^3H$	4	24096. 2	369. 6	0. 90
		5	24465. 8	357. 6	1. 04
		6	24823. 4		1. 14
$4d^4\,5s^2$	$a\,^1S$	0	?24472. 1		
$4d^5(^2I)5s$	$a\,^3I$	5	25516. 9	32. 0	0. 83
		6	25548. 9	89. 7	1. 04
		7	25638. 6		1. 13
$4d^6$	$c\,^5D$	4	*25455. 7	−251. 4	1. 46
		3	*25707. 1	−87. 5	1. 38
		2	*25794. 6	−26. 1	
		1	*25820. 7		
		0	?25980. 3		
$4d^5(^4F)5s$	$a\,^5F$	5	*25905. 5	−91. 7	1. 41
		4	*25997. 3	−192. 2	1. 33
		3	*26189. 4	−146. 4	1. 36
		2	*26335. 8	52. 1	0. 85
		1	*26283. 7		
$4d^5(^4P)5s$	$b\,^3P$	0	26450. 1	−35. 2	
		1	26414. 9	1000. 2	1. 44
		2	27415. 1		
$4d^4\,5s^2$	$a\,^1G$	4	26635. 8		1. 12
$4d^5(^2D)5s$	$b\,^3D$	3	*26638. 8	−119. 9	1. 17
		2	26758. 7	−603. 9	0. 98
		1	27362. 6		
$4d^5(^2aF)5s$	$b\,^3F$	2	27093. 3	+681. 1	
		3	*27774. 4	−8. 7	1. 09
		4	27765. 7		1. 11
$4d^4\,5s^2$	$b\,^3G$	3	27383. 8	−41. 8	0. 93
		4	27342. 0	384. 7	1. 10
		5	27726. 7		1. 21
$4d^5(^2I)5s$	$a\,^1I$	6	28241. 0		1. 00
$4d^5(^2bF)5s$	$c\,^3F$	2	29642. 0	517. 3	
		3	30159. 3	342. 6	1. 09
		4	30501. 9		1. 20
$4d^5(^2H)5s$	$b\,^3H$	4	29842. 2	139. 6	
		5	29981. 8	131. 3	1. 05
		6	30113. 1		1. 11
$4d^4\,5s^2$	$b\,^1I$	6	31484. 6		1. 01
$4d^5(^2G)5s$	$c\,^3G$	3	?31507. 0	3. 4	
		4	31510. 4		
		5			
$4d^5(^2G)5s$	$b\,^1G$	4	32688. 3		0. 99
$4d^5(^2H)5s$	$a\,^1H$	5	33904. 5		1. 00
$4d^6$	$c\,^3H$	6	34810. 2	−101. 9	1. 11
		5	34912. 1	−129. 9	1. 06
		4	35042. 0		0. 77
$4d^6$	$c\,^1I$	6	39521. 1		1. 03

? indicates some uncertainty as to the reality of the level.
* indicates levels known prior to the present investigation.

in Zr II, just as in Mo I. The spectra with $4d$ electrons are thus favorable for the study of configuration interaction in contrast to spectra with $3d$ electrons where effects of configuration interaction are not very pronounced. Mo I is especially favorable because its configurations give rise to a large number of terms; nearly half of these already have been found experimentally, so that the theory can be tested in many instances.

A study of Mo I also furnishes information about polarization effects. A major fact is that the $L(L+1)$ correction, found by Trees to apply in the $3d^54s$ configuration of Fe III [16] is shown to be applicable also in the $4d^55s$ configuration of Mo I. The $L(L+1)$ correction is an empirical one that corresponds rather closely to the difference between theory and experiment in the configurations with $3d$- and $4s$-electrons that have been compared so far with theory [15 to 18]. It represents, therefore, that part of the polarization energy that cannot be accounted for by choosing most favorable values for the radial integrals in the Slater theory.

Racah has pointed out [17] that the validity of a correction of form $L(L+1)$ in d^n (or d^ns) configurations for all n values is evidence that the polarization energy can be treated linearly, just as the electrostatic interaction is considered in the Slater first-order theory. The fact that we obtain good agreement when the $L(L+1)$ correction is used as a linear correction for the strongly interacting configurations of Mo I is additional evidence of the linear behavior of the polarization energy.

The assumptions needed to justify theoretically a linear treatment of second-order effects in Racah's work have not been published, but they would not necessarily justify a linear treatment when configuration interaction is present. Thus a strong demonstration of linearity (or of deviations from linear behavior) in such cases should supply significant new data to check any theory that is developed. However, the $L(L+1)$ correction contributes only about half as much to the term energies in Mo I as it does to the corresponding terms in Fe III. Since the correction is relatively small, the agreement obtained is not very strong evidence for the validity of the linear treatment. It is possible that more definite evidence will be found when the experimental analysis of Mo I has been carried to completion.

The smallness of the $L(L+1)$ correction in Mo I, as compared to Fe III, may be a result of the general tendency of the deviations between theory and experiment to get smaller in the heavier elements.[3] It has already been noted that the magnitude of the correction is fairly constant in spectra of the iron group [17], but no information is available with respect to the variation in magnitude for unrelated spectra. This variation should provide additional fundamental information about the polarization effects.

2. Application of Theory to Analysis of Data

The Slater theory, extended to include effects of configuration interaction, has been checked against experiment in many cases, but is not often used to aid the experimental analysis. In the theoretical calculation, the Slater integrals are regarded as arbitrary parameters and are evaluated to obtain best agreement with the known terms of the spectrum. A minimum number of terms must be known experimentally before the calculation can be started, and this minimum is larger the more parameters there are to be evaluated in the theory. In practice more than the minimum number of terms should be known experimentally, so that inaccuracies in the theory will tend to compensate each other.

The theoretical estimate of term positions can be made more accurate by applying the $L(L+1)$ correction to the Slater theory. By using this correction it is usually possible to predict the positions of terms within limits of ± 400 cm^{-1}, so that the search for new levels can be concentrated to a narrower region of wave numbers than is usually possible without it.

The theoretical calculation, including configuration interaction is discussed in detail in section 4. When completed, it predicted the positions of new terms with good accuracy and also suggested the term designations of the $a\,^1$G and $b\,^3$P terms, whose levels were previously known but unassigned. This calculation led also to the discovery of the $b\,^1$I, $a\,^1$H, $b\,^1$G, $c\,^3$G, and $a\,^1$S terms. The last is of particular interest because it is very highly perturbed and is found within 100 cm^{-1} of the predicted position.

3. Limitations Imposed by Magnetic Interactions

In general, Mo I shows good LS-coupling, and it is possible to group its levels into terms with relatively small intervals and to neglect spin-orbit interaction in the theoretical calculation. The homologous spectrum of Cr I was useful in the experimental analysis in indicating whether terms were regular or inverted and had large or small intervals. However, in a few cases, overlapping of terms in Mo I produces strong magnetic interactions, as indicated by the distortion of the intervals of the terms and by the mixing of the g-values of the interacting levels. In such cases, the determination of the L- and S-values of the levels is difficult, and the assignments given may be partly arbitrary, just as the assignment of a configuration and a parent term may be partly arbitrary when the configuration interaction is strong. Qualitative estimates of the effects can be made by examining the term intervals and the g-values.

The clearest example appears in the interaction between the $a\,^3$D and $a\,^3$P terms. If we assume that the $a\,^3\mathrm{P}_0$ and $a\,^3\mathrm{D}_3$ levels are relatively unperturbed, the large intervals between the level $a\,^3\mathrm{P}_0$ and the levels $a\,^3\mathrm{P}_1$ and $a\,^3\mathrm{P}_2$, and between the level $a\,^3\mathrm{D}_3$ and the levels $a\,^3\mathrm{D}_1$ and $a\,^3\mathrm{D}_2$ indicate that the $a\,^3\mathrm{P}_1$ and $a\,^3\mathrm{P}_2$ levels have been pushed up, whereas the $a\,^3\mathrm{D}_1$ and $a\,^3D_2$ levels have been depressed by their mutual interaction. The matrix elements of these interactions are shown in Appendix 2 to be of the correct order of magnitude to produce the observed effect.

The interaction between the $a\,^3\mathrm{D}_1$ and $a\,^3\mathrm{P}_1$ levels is also shown by g-sharing. The respective observed and predicted g-values for $a\,^3\mathrm{P}_1$ are 0.95 and 1.50, and for $a\,^3\mathrm{D}_1$ they are 1.04 and 0.50. The sum of the observed g-values for these levels is 1.99, which is very close to 2.00, the sum of the predicted g-values. On the basis of g-values it might be better to interchange the $a\,^3\mathrm{D}_1$ and the $a\,^3\mathrm{P}_1$ levels. The present assignment was made in order to keep the term intervals as small as possible; this assignment also gives better agreement with the multiplet-intensity rules.

Considerable mixing of levels occurs in the region between 26400 and 27800 cm^{-1}, where there are 13 levels belonging to four triplet terms and one singlet term. Because of the strong magnetic interactions between levels, some of the assignments of levels to terms are not definite. Strong g-sharing is found between the levels having $J=3$ and $J=4$, and only the g-sums are preserved.

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[3] Part of the evidence demonstrating this tendency is briefly noted in the first paragraph of reference [19]. The calculations for the heavy elements must be made in intermediate coupling because the magnetic interactions are important.

The mixing of levels due to magnetic interaction affects the way they combine, so that the combination properties also indicate qualitatively the presence of the magnetic interactions. Thus the $b\ ^3F_3$ and $b\ ^3G_3$ levels and also the $b\ ^3F_4$ and $b\ ^3G_4$ levels combine in a very similar manner with most of the same odd levels, and the $a\ ^1S_0$ term combines with most of the levels with which the $a\ ^3P_0$ level combines.

Many combinations with *L*-values differing by 2 or 3 and mlutiplicities differing by 1 or 2 were observed with the few well-identified odd terms that are known. Little has been done toward assigning *L*- and *S*-values to the majority of the odd levels. When that phase of the analysis is carried out, more assistance may be obtained in identifying the even levels by considering combination properties. It is probable that the analysis of the odd levels will be complicated by the presence of magnetic and configuration interactions.

4. Calculated Term Values

The matrices for the energy of terms in the d^6, $d^5\,s$,[3a] and $d^4\,s^2$ configurations are given in Appendix 1. The elements are simple multiples of quantities tabulated by Racah [12]; additional details are given in reference [15]. The classification of terms in a configuration d^n must be amplified to distinguish between terms with the same *S*- and *L*-values, and Racah's classification in terms of seniority number has been used in setting up the matrices of Appendix 1 (the prefixed subscripts indicate the seniority number). A fact of importance in understanding this classification is that a term in the $d^5\,s$ configuration is usually characterized by a single seniority number that differentiates terms with the same *S*- and *L*-values. Terms of the same *S*- and *L*-values in the $d^4\,s^2$ and d^6 configurations are not characterized by a single seniority number because there is a nonzero, nondiagonal element in that part of the matrix of Appendix 1 that refers to the single configuration being considered. The $L(L+1)$ correction [16] has not been included in these matrices; to include it a term $\alpha L(L+1)$ must be added to each element in the main diagonal.

The method used to evaluate the parameters is considerably simpler than the usual method [13]; it has been given in detail with the idea that it may help in future applications of the theory to the analysis of experimental data. Although the procedure is probably generally applicable, it is justified chiefly by the good over-all agreement obtained in the final result.

4.1. Radial Parameters for the $4d^5$ 5s Configuration

In the $d^5\,s$ configuration the five parameters, *A*, *B*, *C*, G_2, and α, must be evaluated. This is done with the seven observed levels that are not perturbed by configuration interaction, and the three additional observed terms that enter into the 3×3 matrices.[4] The last three observed values were corrected for the effects of configuration interaction before inclusion in the analysis.[5]

The value $G_2=1{,}795$ is taken as one-sixth the separation between the $a\ ^7S$ and $a\ ^5S$ terms. These two terms are usually well separated from other terms that can interact with them magnetically, and any magnetic interactions present will have a minimum effect on the value of G_2 because of the large mutual separation of the ^7S and ^5S terms. It is assumed that G_2 values obtained from the separations of pairs of terms based on the same d^5 parent will be consistent in the absence of configuration interaction and magnetic effects [16].

The 10 observed values are then used in a least-squares calculation to get the best values of *A*, *B*, *C*, and α. It should be pointed out that if only terms with seniority number 5 in the d^5 parent term had been selected, α could not have been evaluated because its effect could be absorbed in the values of *A*, *B*, and *C*. The details are closely similar to those pointed out for the terms with seniority number 4 in the d^4 and d^6 configurations [18]. Six of the 10 terms used in the parameter evaluation have parent terms with seniority number 5, and four have parent terms with seniority number 3.

In table 2 the term values are calculated without the $L(L+1)$ correction in the two columns headed (1); the mean deviation between theory and experiment is ±416 cm^{-1}. In the columns headed (2), the calculation is given with the $L(L+1)$ correction, and the mean deviation is reduced to ±170 cm^{-1}. The latter agreement is probably as good as can be expected when magnetic interactions are neglected, as the discussion in Appendix 2 indicates.

TABLE 2.—*Term values in $4d^5$ 5s configuration of* Mo I

Term	Obs.	(1)[a]		(2)[b]	
		Calc.	Diff.	Calc.	Diff.
$4d^5(a\ ^6S)5s\ a\ ^7S$	0	−153	−153	−95	−95
$4d^5(a\ ^6S)5s\ a\ ^5S$	10768	10617	−151	10675	−93
$4d^5(a\ ^4G)5s\ a\ ^5G$	16747	16557	−190	16830	83
$4d^5(a\ ^4P)5s\ a\ ^5P$	18322	19226	904	18478	156
$4d^5(a\ ^4D)5s\ b\ ^5D$	19846	19854	8	19714	−132
$4d^5(a\ ^2I)5s\ a\ ^3I$	25574	24946	−628	25643	69
$4d^5(a\ ^4F)5s\ a\ ^5F$	26080	26291	211	26178	98
$4d^5(a\ ^2I)5s\ a\ ^1I$	29024	28536	−488	29233	209
$4d^5(a\ ^2H)5s\ b\ ^3H$	30155	29970	−185	29959	−196
$4d^5(a\ ^2H)5s\ a\ ^1H$	33904	33560	−344	33549	−355
Mean deviation-------		±416		±170	
A		25307		25960	
B		471		488	
C		2041		1898	
G_2		1795		1795	
α		--------------		38	

[a] No $L(L+1)$ correction.
[b] With $L(L+1)$ correction.

[3a] A paper by N. Rosenzweig (Phys. Rev. **88**, 580 (1952)) has just appeared that gives the d^6—d^5s matrix elements. Some of his elements differ in sign from the elements in Appendix I; it is believed that the present choice of phase corresponds to that already established by Racah.

[4] These are the terms listed in table 2. The three terms that were corrected are $b\ ^5D$, $a\ ^1I$, and $b\ ^3H$.

[5] It is assumed that the experimentally observed term values are the eigenvalues of the matrices. The nondiagonal elements of the matrices are estimated as closely as possible from considerations similar to those in section 4.3. The corrected observed values are then the diagonal elements that would be required to lead to the assumed eigenvalues. The correction is a function only of the value assumed for the interaction parameter H_2. Because the estimated value $H_2=348$ is not much different from the final evaluation $H_2=357$, the inclusion of these corrected terms in the analysis will not reduce the accuracy.

4.2. Parameters for the $4d^4 5s^2$ and $4d^6$ Configurations and Positions of Unperturbed Terms

It is usually assumed that the parameters are equal in all configurations of the same atom when they are defined by radial integrals having electrons with the same n- and l-values; this is the assumption made by Ufford [11]. To obtain the full agreement possible with the $L(L+1)$ correction, it is necessary to assume that the parameters are independent when they occur in different configurations. To reduce the number of parameters that must be evaluated, it would otherwise have been preferable to use the more usual assumption. Considerations relating to these two approximations have been presented in reference [13].

Only the three terms $c\ ^5\mathrm{D}$, $c\ ^3\mathrm{H}$, and $c\ ^1\mathrm{I}$ are known in the d^6 configuration; these are the terms that enter into the 3×3 matrices and are used to evaluate the d^6 parameters A, B, C, and α. In the $d^4\,s^2$ configuration the corresponding terms $a\ ^5\mathrm{D}$, $a\ ^3\mathrm{H}$, and $b\ ^1\mathrm{I}$ are also known, and these three terms of $d^4\,s^2$ were used to evaluate the four corresponding $d^4\,s^2$ parameters. The method of correction used for the terms in the $d^5\,s$ configuration (see footnote 5) is also used in these two configurations. In either configuration the three terms chosen can be calculated with two independent parameters, each of which is a linear combination of parameters A, B, C, and α.[6] Some confirmation of the theory can therefore be obtained at this stage of the calculation, since two parameters are used to explain three observations. The least-squares calculation is given in table 3. The mean deviation for the $d^4\,s^2$ configuration is ±128 cm^{-1}, and the mean deviation for the d^6 configuration is ±43 cm^{-1}.

TABLE 3.—*Term values in $4d^4\,5s^2$ and $4d^6$ configurations of* Mo I *(cm^{-1})*

Term	Obs.	Calc.	Diff.	Term	Obs.	Calc.	Diff.
$4d^4\,5s^2\ a^5\mathrm{D}$	13506	13442	−64	$4d^6\ c^5\mathrm{D}$	24365	24376	11
$4d^4\,5s^2\ a^3\mathrm{H}$	24996	25170	174	$4d^6\ c^3\mathrm{H}$	34257	34192	−65
$4d^4\,5s^2\ b^1\mathrm{I}$	31156	31034	−122	$4d^6\ c^1\mathrm{I}$	39067	39100	33
Mean deviation---±128				Mean deviation---±43			
A	24850			A	33700		
B	555			B	455		
C	2150			C	1771		
α	38			α	38		

To obtain values of all four parameters it was necessary to make two assumptions. The first of these is that $\alpha=38$ in the $d^4\,s^2$ and d^6 configurations, which makes the value of α agree with the value already determined in the $d^5\,s$ configuration [17, 18]. Because the $L(L+1)$ correction does not apply as well in the $d^4\,s^2$ and d^6 configurations [18], it is hard to give a general procedure for evaluating α in these configurations. In Mo I, however, the fact that α is small makes errors in evaluating it less important, so that this first assumption should lead to little error. The second assumption made was that the ratio of F_4 to F_2 (or of B to C) is the same as the ratio already determined in the $d^5\,s$ configuration. This assumption should also be fairly good because in published calculations for the spectra of the Fe group of elements [13 to 16] the ratio F_4/F_2 is fairly constant and is usually within the limits 0.068 ±0.003, despite the fact that the different configurations occur in different atoms and that the assumptions used in the calculations differ slightly. The value of the ratio already obtained in the $d^5\,s$ configuration of Mo I ($F_4/F_2=0.0714$) agrees with the value of the ratio found by Ufford [11] in the d^3 and $d^2\,s$ configurations of Zr II ($F_4/F_2=0.0715$); this is some confirmation of the constancy of this ratio in spectra with $4d$ electrons.

In the columns of table 4 headed (1) are given the positions of the terms calculated with the parameters evaluated in this and section 4.1. The mean deviation of ±2391 cm^{-1} will be largely explained in the following section, when the effects of configuration interaction are considered. Besides indicating the magnitude of the configuration interaction, the unperturbed positions of the terms determine the configuration and parent of the observed terms (whenever either of these is uncertain), as outlined in section 4.4.

4.3. Interaction Parameters: Term Values With Configuration Interaction

Three parameters are required to define the elements of configuration interaction. Two parameters, representing interaction between the $d^5\,s$ and d^6, and between the $d^5\,s$ and $d^4\,s^2$ configurations, are defined by radial integrals H_2, whose single electron wave functions have identical n and l values, and these parameters were therefore considered equal. The third interaction parameter, G_2, originates in the interaction between the d^6 and $d^4\,s^2$ configurations and was assumed equal to the parameter G_2 already determined in the $d^5\,s$ configuration, since the two parameters are defined similarly. With these assumptions, only one parameter, H_2, is needed to include the effects of configuration interaction in the calculation. When more terms are known experimentally, it may be possible to check these assumptions. The agreement obtained with the terms that are known at present does not seem to depend very critically on the values assumed for the radial parameters in the interaction elements between terms of the d^6 and either the $d^5\,s$ or $d^4\,s^2$ configurations, and the assumptions are really approximations for the values of the two parameters entering into these interactions.

The parameter H_2 can be evaluated, so that exact agreement with any one experimental value is obtained by finding linear formulas for the eigenvalues of the matrix [13]; the iteration procedure is convenient for finding the eigenvector needed in making this calculation.[7] Because H_2 is determined

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[6] It can easily be verified from the formula in Appendix 1 that the energies are given by the formulas: $^5\mathrm{D}=X-21Y$; $^3\mathrm{H}=X-17Y$; $^1\mathrm{I}=X-15Y$; where $X=A+21C+132\alpha$; $Y=B+C+6\alpha$.

[7] W. J. Duncan and A. R. Collar, Phil. Mag. **17**, 865 (1934). A constant larger than half the sum of the least and greatest eigenvalues should be subtracted from each element of the main diagonal in iterating for the lowest eigenvalue.

TABLE 4. *Term values in* Mo I (cm^{-1})

Term	Obs.	(1)[a]		(2)[b]	
		Calc.	Diff.	Calc.	Diff.
$4d^5(a\,^6S)5s$ $a\,^7S$	0	−95	−95	−95	−95
$4d^5(a\,^6S)5s$ $a\,^5S$	10768	10675	−93	10675	−93
$4d^4\,5s^2$ $a\,^5D$	11832	13423	1591	11602	−230
$4d^5(a\,^4G)5s$ $a\,^5G$	16747	16830	83	16830	83
$4d^5(a\,^4P)5s$ $a\,^5P$	18322	18478	156	18478	156
$4d^5(a\,^4D)5s$ $b\,^5D$	20226	19714	−512	20066	−160
$4d^5(a\,^4G)5s$ $a\,^3G$	21178	24010	2832	21187	9
$4d^4(a\,^4D)5s$ $a\,^3D$	21258	26894	5636	21352	94
$4d^4\,5s^2$ $a\,^3P$	22413	25405	2992	21529	−884
$4d^4\,5s^2$ $a\,^3F$	23571	26094	2523	23575	4
$4d^4\,5s^2$ $a\,^1S$	24472	33194	8722	24464	−8
$4d^4\,5s^2$ $a\,^3H$	24506	25155	649	24654	148
$4d^5(a\,^2I)5s$ $a\,^3I$	25574	25643	69	25643	69
$4d^6$ $c\,^5D$	25659	24373	−1286	25842	183
$4d^5(a\,^4F)5s$ $a\,^5F$	26080	26178	98	26178	98
$4d^4\,5s^2$ $a\,^1G$	26636	31128	4492	26509	−127
$4d^5(a\,^2D)5s$ $b\,^3D$	26824	27130	306	26988	164
$4d^5(a\,^4P)5s$ $b\,^3P$	26974	25658	−1316	27297	323
$4d^4\,5s^2$ $b\,^3G$	27510	27550	40	27465	−45
$4d^5(a\,^2F)5s$ $b\,^3F$	27608	27811	203	26820	−788
$4d^5(a\,^2I)5s$ $a\,^1I$	28241	29233	992	28378	137
$4d^5(a\,^2H)5s$ $b\,^3H$	29995	29959	−36	29756	−239
$4d^5(a\,^2F)5s$ $a\,^1F$		31401		29069	
$4d^5(a\,^2D)5s$ $a\,^1D$		30720		30484	
$4d^5(b\,^2F)5s$ $c\,^3F$	30183	31823	1640	29870	−313
$4d^4\,5s^2$ $b\,^1I$	31485	31021	−464	31418	−67
$4d^5(a\,^2G)5s$ $c\,^3G$	31510	30175	−1335	31369	−141
$4d^5(b\,^2F)5s$ $b\,^1F$		35413		31550	
$4d^5(a\,^2G)5s$ $b\,^1G$	32688	33765	1077	32404	−284
$4d^4\,5s^2$ $c\,^3D$		30903		32924	
$4d^6$ $c\,^3P$		34211		33249	
$4d^5(a\,^2H)5s$ $a\,^1H$	33904	33549	−355	33549	−355
$4d^5(a\,^4F)5s$ $d\,^3F$		33358		34020	
$4d^4\,5s^2$ $b\,^1D$		34723		33585	
$4d^5(a\,^2S)5s$ $a\,^3S$		34295		34295	
$4d^6$ $c\,^3H$	34907	34189	−718	34893	−14
$4d^6$ $d\,^3G$		36084		37005	
$4d^6$ $e\,^3F$		34840		37291	
$4d^5(a\,^2S)5s$ $b\,^1S$		37885		37359	
$4d^5(b\,^2D)5s$ $d\,^3D$		37831		37812	
$4d^5(b\,^2D)5s$ $c\,^1D$		41421		38045	
$4d^6$ $c\,^1I$	39521	39097	−424	39555	34
$4d^6$ $c\,^1G$		39043		40945	
$4d^6$ $e\,^3D$		38737		41832	
$4d^4\,5s^2$ $c\,^1F$		38206		41900	
$4d^4\,5s^2$ $d\,^3P$		42547		42133	
$4d^6$ $d\,^1D$		41891		42411	
$4d^5(b\,^2G)5s$ $e\,^3G$		41779		42572	
$4d^4\,5s^2$ $f\,^3F$		42618		43489	
$4d^5(b\,^2G)5s$ $d\,^1G$		45369		47025	
$4d^6$ $d\,^1F$		44782		47283	
$4d^6$ $e\,^3P$		48272		47758	
$4d^4\,5s^2$ $e\,^1G$		46792		47786	
$4d^6$ $c\,^1S$		40605		48757	
$4d^6$ $g\,^3F$		48404		49882	
$4d^5(a\,^2P)5s$ $a\,^1P$		52981		52981	
$4d^6$ $f\,^1G$		51893		53320	
$4d^5(a\,^2P)5s$ $f\,^3P$		49391		53518	
$4d^5(c\,^2D)5s$ $f\,^3D$		53304		53891	
$4d^5(c\,^2D)5s$ $e\,^1D$		56894		55524	
$4d^4\,5s^2$ $f\,^1D$		57673		60044	
$4d^6$ $g\,^1D$		60721		63947	
$4d^4\,5s^2$ $d\,^1S$		70606		68640	
$4d^6$ $e\,^1S$		71315		74385	
Mean deviation--------		±2391 cm^{-1}		±273 cm^{-1}	

Configuration	*A*	*B*	*C*	G_2	α
$4d^4\,5s^2$	24850	555	2150	1795	38
$4d^5\,5s$	25960	488	1898		38
$4d^6$	33700	455	1771		38

Interaction parameters
$H_2=357.3$ $G_2=1795$

[a] No configuration interaction.
[b] With configuration interaction.

most accurately from the terms that show large effects of configuration interaction, it was evaluated for only such terms. The values of H_2 determined from $a\,^3$G, $a\,^3$D, $a\,^3$P, $a\,^3$F, and $a\,^1$G are 358, 362, 286, 358, and 350 cm^{-1}, respectively. The consistency of these values is a very good check on the theory, particularly when it is noted that the low value for $a\,^3$P can be explained by consideration of magnetic effects (Appendix 2). If the term $a\,^3$P is omitted, the average of the other four terms leads to the value $H_2=357$ ($10^{\frac{1}{2}}H_2=1130$ was used in the calculations).

The columns of table 4 headed (2) give the term values calculated with configuration interaction included, by using the values of the parameters determined in this and the two preceding sections.[8] The mean deviation between theory and experiment is ±273 cm^{-1}; by omitting the $a\,^3$P term, it is ±222 cm^{-1}. The $b\,^3$F term also shows a large error, which may not be magnetic in origin; the source of this error is unknown. If this term also is omitted, the mean deviation for the other 27 terms is reduced to ±168 cm^{-1}, which is the mean deviation most representative of the over-all agreement obtained.

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[8] The characteristic equation for the eigenvalues was determined by the Danielewsky method as described by H. Wayland, Quart. Applied Math. **2**, 277 (1944). It took 6 to 8 hours to find the eigenvalues of a 6×6 matrix in this way with a desk calculator. Many of the values obtained were checked against values obtained with the iteration procedure. The agreement obtained sets a limit of ±2 cm^{-1} on the error in the calculation of the eigenvalues.

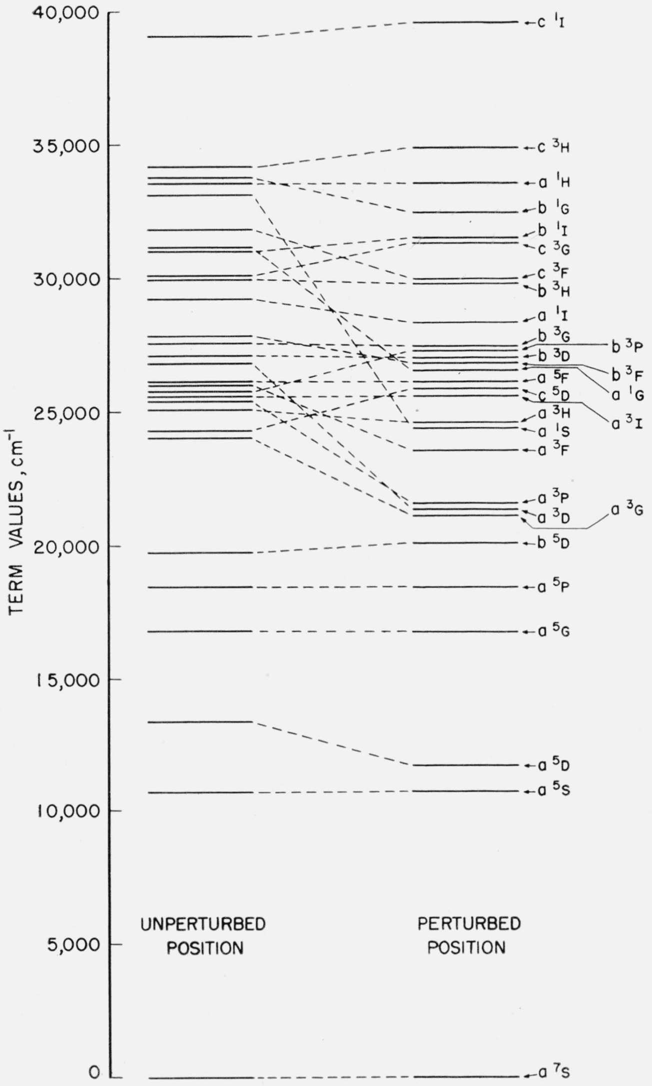

FIGURE 1. *Effect of configuration interaction in* Mo I.

The best confirmation of the theory comes from the fact that seven of the eight observed values not used to determine the parameters were predicted within limits of twice the mean deviation (that is, within the limits ±336 cm^{-1}). Several other levels used in evaluating parameters could have been omitted without any loss in accuracy, as the preliminary calculation showed. The calculated term values under the headings (1) and (2) of table 4 are compared graphically in figure 1 (only those terms that have been experimentally observed are shown).

4.4. Classification of Terms

An indication of the importance of configuration interaction is obtained from the value of the parameter H_2. The value of this parameter, 357, (see section 4.3) is large compared to values so far found in spectra with $3d$ and $4s$ electrons. (The largest value, $H_2=172$, is found in Ti II [13]). The strong configuration interaction in Mo I leads to such complete mixing that it is not possible in many cases to determine experimentally the configuration, or, in the case of d^5s terms, the parent to which a term belongs. The configuration and the parent term are specified theoretically in such cases by naming the terms of same S- and L-value, so that the order is the same as that of the unperturbed term values. This method of classification depends on the values assumed for the parameters in calculating the unperturbed positions of the terms, and when two terms have unperturbed positions that are very close together, there may be some indeterminacy in the naming of terms according to this rule. For instance, the $a\,^3$D and $b\,^3$D terms are separated by 236 cm^{-1} and the $a\,^3$P and $b\,^3$P terms are separated by 253 cm^{-1} in the unperturbed positions, and these differences are the same order of magnitude as the mean deviation of the final calculation.

Another shortcoming of this method of classification is that the name of the term may have little physical significance. When the configuration interaction is weak, the dominant component of the eigenfunction is indicated, but this need not be the case when the configuration interaction is strong. The percentage compositions of the three lowest ^{3}D levels and the three lowest ^{3}P levels are given in table 5 as representative examples. It will be noted that if the classification were made to correspond to the dominant component of the eigenfunction, the assignments for $a\,^3$D and $b\,^3$D and for $a\,^3$P and $b\,^3$P would be reversed. This sort of discrepancy will generally not arise when the unperturbed levels are well separated, as is the case for $c\,^3$D and $c\,^3$P. It is expected that naming a term from the dominant component of the eigenfunction depends too critically on the values assumed for the radial parameters to make this method of classification any more significant. A determination of the eigenvectors of all the terms would entail considerable additional work, and this is another disadvantage of such a classification.

TABLE 5.—*Composition of lowest* ^{3}P *and* ^{3}D *states of* Mo I

Observed term	Pure term with no configuration interaction					
	$d^4\,s^2\,^3P-$	$d^5(^4P)s\,^3P$	$d^6\,^3P-$	$d^4\,s^2\,^3P+$	$d^6\,^3P+$	$d^5(^2P)s\,^3P$
$a\,^3$P	43.6	52.3	3.6	0.3	0.0	0.2
$b\,^3$P	53.0	37.7	3.3	1.2	3.8	1.0
$c\,^3$P	0.3	2.4	74.5	16.6	1.6	4.6
	$d^5(^4D)s\,^3D$	$d^5(^2D^-)s\,^3D$	$d^4\,s^2\,^3D$	$d^5(^2D)s\,^3D$	$d^6\,^3D$	$d^5(^2D^+)s\,^3D$
$a\,^3$D	26.1	36.8	27.6	0.1	9.1	0.3
$b\,^3$D	59.3	40.7	0.0	.0	0.0	.0
$c\,^3$D	6.5	10.4	55.0	20.3	7.5	.3

This work has been carried out in the Spectroscopy Section of the National Bureau of Standards. W. F. Meggers, Chief of this Section, has given it his wholehearted support. C. C. Kiess, who suggested this problem, has given generously of his time and valuable advice throughout the course of the work. It is a pleasure to express to them our gratitude for their interest and expert guidance.

5. Appendix 1. Matrices of Electrostatic Repulsion

Term energies for d^6, d^5s, and $d^4\,s^2$ configurations. $B=F_2-5F_4$; $C=35F_4$; $H=\sqrt{10}H_2=(\sqrt{10}/35)\,R^2(dd,ds)$

$d^6\ {}^1_2\mathrm{S}$	$A+14B+14C$	$6\sqrt{21}B$	0	$-2G_2$	0
$d^6\ {}^1_4\mathrm{S}$	$6\sqrt{21}B$	$A+6B+6C$	$-8H$	0	G_2
$d^5({}^2_5\mathrm{S})s\ {}^1\mathrm{S}$	0	$-8H$	$A-3B+8C-G_2$	0	$8H$
$d^4\ s^2\ {}^1_2\mathrm{S}$	$-2G_2$	0	0	$A+14B+14C$	$6\sqrt{21}B$
$d^4\ s^2\ {}^1_4\mathrm{S}$	0	G_2	$8H$	$6\sqrt{21}B$	$A+6B+6C$

$d^5({}^2_5\mathrm{S})s\ {}^3\mathrm{S}$	$A-3B+8C-3G$
$d^5({}^6_5\mathrm{S})s\ {}^5\mathrm{S}$	$A-35B+G_2$
$d^5({}^6_5\mathrm{S})s\ {}^7\mathrm{S}$	$A-35B-5G_2$
$d^5({}^2_3\mathrm{P})s\ {}^1\mathrm{P}$	$A+20B+10C-G_2$

$d^6\ {}^3_2\mathrm{P}$	$A-7B+7C$	$4\sqrt{14}B$	$-\sqrt{14}H$	0	$-2G_2$	0
$d^6\ {}^3_4\mathrm{P}$	$4\sqrt{14}B$	$A-3B+4C$	$-H$	$\sqrt{14}H$	0	G_2
$d^5({}^2_3\mathrm{P})s\ {}^3\mathrm{P}$	$-\sqrt{14}H$	$-H$	$A+20B+10C-3G_2$	0	$-\sqrt{14}H$	$-H$
$d^5({}^4_3\mathrm{P})s\ {}^3\mathrm{P}$	0	$\sqrt{14}H$	0	$A-28B+7C$	0	$\sqrt{14}H$
$d^4\ s^2\ {}^3_2\mathrm{P}$	$-2G_2$	0	$-\sqrt{14}H$	0	$A-7B+7C$	$4\sqrt{14}B$
$d^4\ s^2\ {}^3_4\mathrm{P}$	0	G_2	$-H$	$\sqrt{14}H$	$4\sqrt{14}B$	$A-3B+4C$

$d^5({}^4_3\mathrm{P})s\ {}^5\mathrm{P}$	$A-28B+7C-4G_2$

Term energies for d^6, d^5s, *and* $d^4\,s^2$ *configurations.* $B=F_2-5F_4$; $C=35F_4$; $H=\sqrt{10}H_2=(\sqrt{10}/35)R^2(dd,ds)$—Continued

$d^6\ {}^1_2\mathrm{D}$	$A+15B+9C$	$12\sqrt{2}B$	$\sqrt{7}H$	0	$3H$	$-2G_2$	0
$d^6\ {}^1_4\mathrm{D}$	$12\sqrt{2}B$	$A+3B+6C$	0	H	$3\sqrt{2}H$	0	G_2
$d^5({}^2_1\mathrm{D})s\ {}^1\mathrm{D}$	$\sqrt{7}H$	0	$A+14C-G_2$	$-6\sqrt{14}B$	0	$-\sqrt{7}H$	0
$d^5({}^2_5\mathrm{D})s\ {}^1\mathrm{D}$	0	H	$-6\sqrt{14}B$	$A-6B+8C-G_2$	0	0	$-H$
$d^5({}^2_3\mathrm{D})s\ {}^1\mathrm{D}$	$3H$	$3\sqrt{2}H$	0	0	$A-4B+10C-G_2$	$3H$	$3\sqrt{2}H$
$d^4\ s^2\ {}^1_2\mathrm{D}$	$-2G_2$	0	$-\sqrt{7}H$	0	$3H$	$A+15B+9C$	$12\sqrt{2}B$
$d^4\ s^2\ {}^1_4\mathrm{D}$	0	G_2	0	$-H$	$3\sqrt{2}H$	$12\sqrt{2}B$	$A+3B+6C$

$d^6\ {}^3_4\mathrm{D}$	$A+5B+4C$	0	$-3\sqrt{2}H$	$-2H$	$3H$	G_2
$d^5({}^2_1\mathrm{D})s\ {}^3\mathrm{D}$	0	$A+14C-3G_2$	$-6\sqrt{14}B$	0	0	0
$d^5({}^2_5\mathrm{D})s\ {}^3\mathrm{D}$	$-3\sqrt{2}H$	$-6\sqrt{14}B$	$A-6B+8C-3G_2$	0	0	$3\sqrt{2}H$
$d^5({}^2_3\mathrm{D})s\ {}^3\mathrm{D}$	$-2H$	0	0	$A-4B+10C-3G_2$	0	$-2H$
$d^5({}^4_5\mathrm{D})s\ {}^3\mathrm{D}$	$3H$	0	0	0	$A-18B+5C$	$-3H$
$d^4\ s^2\ {}^3_4\mathrm{D}$	G_2	0	$3\sqrt{2}H$	$-2H$	$-3H$	$A-5B+4C$

Term energies for d^6, d^5s, *and* $d^4\,s^2$ *configurations.* $B=F_2-5F_4$; $C=35F_4$; $H=\sqrt{10}H_2=(\sqrt{10}/35)\,R^2(dd,ds)$—Continued

$d^6\,{}^{5}_{4}\mathrm{D}$	$A-21B$	$-\sqrt{7}H$	G_2
$d^5({}^{4}_{5}\mathrm{D})s\,{}^5\mathrm{D}$	$-\sqrt{7}H$	$A-18B+5C-4G_2$	$\sqrt{7}H$
$d^4\,\mathrm{s}^2\,{}^{5}_{4}\mathrm{D}$	G_2	$\sqrt{7}H$	$A-21B$

$d^6\,{}^{1}_{4}\mathrm{F}$	$A+6C$	$-\frac{3}{2}\sqrt{5}H$	$-\frac{7}{2}H$	G_2
$d^5({}^{2}_{3}\mathrm{F})s\,{}^1\mathrm{F}$	$-\frac{3}{2}\sqrt{5}H$	$A-25B+10\mathrm{C}-G_2$	0	$-\frac{3}{2}\sqrt{5}H$
$d^5({}^{2}_{5}\mathrm{F})s\,{}^1\mathrm{F}$	$-\frac{7}{2}H$	0	$A-9B+BC-G_2$	$\frac{7}{2}H$
$d^4\,s^2\,{}^{1}_{4}\mathrm{F}$	G_2	$-\frac{3}{2}\sqrt{5}H$	$\frac{7}{2}H$	$A+6C$

$d^6\,{}^{3}_{2}\mathrm{F}$	$A-2B+7C$	$12B$	$2H$	0	0	$-2G_2$	0
$d^6\,{}^{3}_{4}\mathrm{F}$	$12B$	$A-8B+4C$	$\frac{3}{2}H$	$-2H$	$\frac{3}{2}\sqrt{5}H$	0	G_2
$d^5({}^{2}_{3}\mathrm{F})s\,{}^3\mathrm{F}$	$2H$	$\frac{3}{2}\mathrm{H}$	$A-25B+$ $10C-3G_2$	0	0	$2H$	$\frac{3}{2}H$
$d^5({}^{4}_{3}\mathrm{F})s\,{}^3\mathrm{F}$	0	$-2H$	0	$A-13B+7C$	0	0	$-2H$
$d^5({}^{2}_{5}\mathrm{F})s\,{}^3\mathrm{F}$	0	$\frac{3}{2}\sqrt{5}H$	0	0	$A-9B+$ $8C-3G_2$	0	$-\frac{3}{2}\sqrt{5}H$
$d^4\,s^2\,{}^{3}_{2}\mathrm{F}$	$-2G_2$	0	$2H$	0	0	$A-2B+7C$	$12B$
$d^4\,s^2\,{}^{3}_{4}\mathrm{F}$	0	G_2	$\frac{3}{2}H$	$-2H$	$-\frac{3}{2}\sqrt{5}H$	$12B$	$A-8B+4C$

Term energies for d^6, d^5s, and $d^4\,s^2$ configurations. $B=F_2-5F_4$; $C=35F_4$; $H=\sqrt{10}H_2=(\sqrt{10}/35)\,R^2(dd,ds)$—Continued

$d^5({}^4_3\mathrm{F})s\ {}^5\mathrm{F}$ $A-13B+7C-4G_2$

$d^6\ {}^1_2\mathrm{G}$	$A-6B+9C$	$4\sqrt{11}B$	$-\frac{1}{3}\sqrt{60}H$	0	$-2G_2$	0
$d^6\ {}^1_4\mathrm{G}$	$4\sqrt{11}B$	$A-4B+6C$	$\frac{1}{12}\sqrt{660}H$	$\frac{9}{2}H$	0	G_2
$d^5({}^2_3\mathrm{G})s\ {}^1\mathrm{G}$	$-\frac{1}{3}\sqrt{60}H$	$\frac{1}{12}\sqrt{660}H$	$A+3B+10C-G_2$	0	$-\frac{1}{3}\sqrt{60}H$	$\frac{1}{12}\sqrt{660}H$
$d^5({}^2_5\mathrm{G})s\ {}^1\mathrm{G}$	0	$\frac{9}{2}H$	0	$A-13B+8C-G_2$	0	$-\frac{9}{2}H$
$d_4\ s^2\ {}^1_2\mathrm{G}$	$-2G_2$	0	$-\frac{1}{3}\sqrt{60}H$	0	$A-6B+9C$	$4\sqrt{11}B$
$d^4\ s^2\ {}^1_4\mathrm{G}$	0	G_2	$\frac{1}{12}\sqrt{660}H$	$-\frac{9}{2}H$	$4\sqrt{11}B$	$A-4B+6C$

$d^6\ {}^3_4\mathrm{G}$	$A-12B+4C$	$\frac{3}{2}H$	$-\frac{1}{12}\sqrt{660}H$	$-\frac{1}{3}\sqrt{60}H$	G_2
$d^5({}^2_3\mathrm{G})s\ {}^3\mathrm{G}$	$\frac{3}{2}H$	$A+3B+10C-3G_2$	0	0	$\frac{3}{2}H$
$d^5({}^2_5\mathrm{G})s\ {}^3\mathrm{G}$	$-\frac{1}{12}\sqrt{660}H$	0	$A-13B+8C-3G_2$	0	$\frac{1}{12}\sqrt{660}H$
$d^5({}^4_5\mathrm{G})s\ {}^3\mathrm{G}$	$-\frac{1}{3}\sqrt{60}H$	0	0	$A-25B+5C$	$\frac{1}{3}\sqrt{60}H$
$d^4\ s^2\ {}^3_4\mathrm{G}$	G_2	$\frac{3}{2}H$	$\frac{1}{12}\sqrt{660}H$	$\frac{1}{3}\sqrt{60}H$	$A-12B+4C$

$d^5({}^4_5\mathrm{G})s\ {}^5\mathrm{G}$ $A-25B+5C-4G_2$

$d^5({}^2_3\mathrm{H})s\ {}^1\mathrm{H}$ $A-22B+10C-G_2$

Term energies for d^6, d^5s, and $d^4\,s^2$ configurations. $B=F_2-5F_4$; $C=35F_4$; $H=\sqrt{10}H_2=(\sqrt{10}/35)R^2(dd,ds)$—Continued

$d^6\,{}^3_4\mathrm{H}$	$A-17B+4C$	$-H$	G_2
$d^5({}^2_3\mathrm{H})s\;{}^3\mathrm{H}$	$-H$	$A-22B+10C-3G_2$	$-H$
$d^4\,s^2\,{}^3_4\mathrm{H}$	G_2	$-H$	$A-17B+4C$

$d^6\,{}^1_4\mathrm{I}$	$A-15B+6C$	$-H$	G_2
$d^5({}^2_5\mathrm{I})s\;{}^1\mathrm{I}$	$-H$	$A-24B+8C-G_2$	H
$d^4\,s^2\,{}^1_4\mathrm{I}$	G_2	H	$A-15B+6C$

$d^5({}^2_5\mathrm{I})s\;{}^3\mathrm{I}$	$A-24B+8C-3G_2$

Appendix 2. Spin-Orbit Interaction

The matrix element of the $a\,{}^3\mathrm{D}-a\,{}^3\mathrm{P}$ interaction is

$$.415\;\zeta(d^4\,s^2)+1.031\;\zeta(d^5\,s)-.065\;\zeta(d^6)$$

for the levels with $J=2$, and 0.745 times this value for those with $J=1$. The value of the radial parameter for spin-orbit interaction can be determined with fair accuracy in the $d^4\,s^2$ configuration from the over-all separation of the $a\,{}^5\mathrm{D}$ levels. By including a correction for the effect of configuration interaction, this leads to a value $\zeta(d^4\,s^2)=715$ cm^{-1}. (The value of ζ in the d^6 configuration cannot be easily determined in this way, but indications are that it is considerably smaller.) If the value 715 cm^{-1} is used for the parameter in all configurations, the matrix element between the levels having $J=2$ is 987 cm^{-1}, and the element between those with $J=1$ is 735 cm^{-1}. Since these values are the order of half the observed separation between the corresponding pairs of levels, the larger part of the observed separation is probably due to the spin-orbit interaction. This conclusion is well confirmed by inspection of the intervals of $a\,{}^3\mathrm{D}$ and $a\,{}^3\mathrm{P}$ and by consideration of the g-values as already indicated in section 3.

The observed term values in table 4 are weighted averages of the actual observed levels. The weighting factor is $2J+1$ so that perturbations of the levels with largest J value are most important in considering the effects of spin-orbit interaction. The considerations of the previous paragraph indicate that the value calculated for $a\,{}^3\mathrm{P}$ should be increased by say 550 cm^{-1}; owing to the $2J+1$ weighting, the $a\,{}^3\mathrm{D}$ value would be decreased by only 3/5 of this value, or by 330 cm^{-1}. The error in the $a\,{}^3\mathrm{P}$ calculation would then be reduced from -884 cm^{-1} to -334 cm^{-1}, while the error for the $a\,{}^3\mathrm{D}$ term would be changed from $+94$ cm^{-1} to -236 cm^{-1}. A quantitative estimate of the effect would require consideration of the interactions with other levels that are farther away and a better estimate of the values of ζ.

The possibility that other large spin-orbit interactions have produced an accidental good agreement has not been fully investigated. However, qualitative estimates of the magnetic effects were made to explain the observed intervals by taking into account the separations of the possible interacting levels and the g-values. A fairly complete and consistent estimate of the effects was obtained which indicated that agreement was not due to accidental cancellation of errors. However, the magnetic interaction is fairly strong and, generally, agreement between theory and experiment better than ±100 cm^{-1} would have to be considered accidental; in certain cases, errors as large as 200 to 300 cm^{-1} could result.

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