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The Configurations $4d^n + 4d^{n-1}5s$ in Doubly-Ionized Atoms of the Palladium Group*

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Four hundred and eighty-three energy levels belonging to the low even configurations of the third spectra of the palladium group are predicted by the use of interpolation formulas for the interaction parameters.

Key Words: Configurations $4d^n+4d^{n-1}5s$, energy levels, interaction parameters, palladium group, theoretical, third spectra.

1. Introduction

In the present paper we describe a systematic treatment of the low even configurations of the sequence [1] of the third spectra of the palladium group. This treatment is analogous to the treatments of the second spectra of the iron group [1],[2] the second spectra of the palladium group [2], and the third spectra of the iron group [3] described in three previous papers.

The approximation used in this work is, as in the the previous papers, the Slater approximation with several improvements. We have included the interaction between the configurations $4d^n$, $4d^{n-1}5s$, we have taken different values for the corresponding parameters B, C and α of the two configurations, we have considered the L(L+1) correction as well as the spin-orbit interaction.

The main stages of this treatment are the following:

(a) The Slater approximation, improved by the above mentioned corrections, is used to calculate the energy levels of each spectrum. After diagonalizing ("Diag.") the energy matrices, the interaction-parameters are considered as free parameters and the best fit to the experimental material is achieved by least-squares calculations ("L.S."). We call this stage "the separate treatment."

(b) The corresponding interaction-parameters of all the spectra of the sequence are expressed as linear functions (in some cases, with a small quadratic correction) of the atomic number. Only the coefficients of these interpolation formulas ("general parameters") retain the role of free parameters. Thus, the whole sequence, containing several hundreds of energy levels, is treated as a single problem ("general treatment") with quite a small number of free parameters.

In the sequence from Y III to Cd III, theory predicts, for the configurations $4d^n+4d^{n-1}5s$, 209 terms which split into 483 levels. Unfortunately, the experimental material is rather scarce. Only 56 terms splitting into 130 levels were found reliable and could be fitted with the calculated levels. In most spectra the number of known terms does not exceed the number of electrostatic-interaction parameters; thus, a separate treatment of one spectrum loses a great deal of its significance. Such separate treatments were performed only as an introduction to the interpolative treatment, which is rather reliable even in this case, since the number of parameters is reduced by the use of interpolation formulas for them.

In the following, we shall first give an account of the situation and the separate calculations in the various spectra, and then describe the general treatment.

Most of the experimental material used in this paper was taken from Moore's Atomic Energy Levels, [4] later referred to as AEL. Unless other sources are explicitly mentioned, it means that the experimental matter was taken from AEL.

2. Notations

The symbols for the parameters are the usual ones. The parameters A, B, C, ζ refer to the configuration d^n, while A′, B′, C′, ζ' refer to the configuration $d^{n-1}s$.

In the actual calculations of the separate treatment A′ was replaced by S′ = A′ − A. In the general treatment A and A′ were replaced by the centers of gravity of the configurations, M and M′, and the difference D′ = M′ − M was expressed by an interpolation formula like the interaction parameters.

The parameter $G=G_2(ds)$ measures the exchange interaction between d and s electrons, $H=R^2(dd, ds)/35$ is the parameter of the interaction between the configurations d^n and $d^{n-1}s$, and α is the parameter of the L(L+1)-correction.

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[1] We call "a sequence" all the atoms belonging to the same period with the same degree of ionization.

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

"Diag." is an abbreviation for "diagonalization," "L.S." is an abbreviation for "least-squares calculation."

3. The Mean Error

Two kinds of mean-error are used in this paper. The "level-mean-error," Δ, is defined by the formula

$$\Delta = \sqrt{\Sigma \Delta_L^2/(n-m)} \tag{1}$$

where the Δ_L are the differences between the observed levels and the calculated levels fitted to them, n is the number of observed levels, and m is the number of free parameters. The "term-mean-error," Δ', (the term, "mean error" as defined in this paper is identical to the concept, "residual standard deviation" used in statistical analysis) is defined by the formula

$$\Delta' = \sqrt{\Sigma \Delta_T^2/(n_T - m_E)} \tag{2}$$

where the Δ_T are the differences between the observed terms and calculated terms fitted to them, n_T is the number of observed terms, and m_E is the number of the free electrostatic parameters.

The calculation of Δ is easier, since our least-squares program furnishes $\Sigma \Delta_L^2$; the abbreviation "mean-error" means the level-mean-error.

In fact, Δ' is a more serious criterion of the precision of our approximations, as the levels belonging to the same term are strongly correlated, while in the definition of Δ they are considered independent.

4. Survey of the Various Spectra

Y III – ($4d+5s$)

This spectrum consists of two terms and needs for its description two electrostatic parameters, so that a separate treatment is meaningless. On the other hand in the general treatment it supplies reliable points for the interpolation formulae of D′ and ζ.

The observed and calculated levels are given in table 7.

Zr III – ($4d^2+4d5s$)

These configurations consist of 7 terms which split into 13 levels. In AEL 6 experimental terms, splitting into 12 levels, are reported; only the ^{1}S of d^2 is unknown.

Here, too, a separate treatment is not fully significant, since 6 electrostatic parameters are necessary. Nevertheless, a separate treatment was performed in order to get some preliminary information about the more stable parameters: D′, B, G, ζ, ζ'.

Initial values for the parameters were taken from Zr II [2]. In L.S. 1, the parameter H was frozen and the mean error was 4 because the number of free electrostatic parameters is equal to the number of known terms.

The parameters of the various stages of the calculation are given in table 1, the observed and calculated energy levels in table 8.

Nb III – ($4d^3+4d^25s$)

In these configurations theory predicts 15 terms which split into 35 levels. In a paper of L. Iglesias [5] 11 experimental terms, splitting into 28 levels are reported.

Parameters for Diag. 1 were prepared by comparison with the parameters of NB II and Zr II [2]. It turned out that the level assigned by Iglesias as $^2D_{3/2}$ is actually the $^2P_{3/2}$ of d^3.

In L.S. 1 we got a mean error of 34.

The estimates of parameters of the various stages of the calculation are given in table 2, the energy levels in table 9.

Mo III – ($4d^4+4d^35s$)

These configurations consist of 27 terms, which split into 72 levels. In AEL only the level $^5D_4$ and the 5 levels belonging to the ^{5}F of d^3s are reported. Since the ground level $d^4\,{}^5D_0$ is unknown, Rico and Catalan estimated the value of the $^5D_4$ to be 1500 cm^{-1}, and added to all the known levels an unknown additive constant x. (Note, there is no connection between the unknown numerical constant "x", introduced by Rico and Catalan, and the variable $x=n-6$ defined in eq (5a) in the section on the interpolative treatment.)

Because of these circumstances we did not even include Mo III in the General Least Squares (G.L.S.) calculation, but, using the improved coefficients of the interpolation formulae achieved in the G.L.S., we calculated the interaction parameters of Mo III. Then the matrices of d^4+d^3s were diagonalized with the use of the interpolated parameters, and thus, we obtained predictions for the levels of Mo III.

Using the calculated values of the (^{4}F)^{5}F one gets for x the value 340. For $^5D_4$ we got the value 1807 cm^{-1} and this gives $x=307$. We suppose that the uncertainty of x is of the order of magnitude of the term-mean-error of the G.L.S. which is 91 cm^{-1}.

The predicted levels of Mo III are given in table 10.

Tc III – ($4d^5+4d^45s$)

In these configurations theory predicts 40 terms which split into 100 levels. Unfortunately, no level was observed. Using the results of the G.L.S. the interaction parameters of Tc III were interpolated, and then the energy matrices of these configurations were diagonalized. In this way the energy levels could be calculated.

The predicted levels of Tc III are given in table 11.

Ru III – ($4d^6+4d^55s$)

These configurations consist of 48 terms, which split into 108 levels. In AEL only 7 levels are reported: The ^{5}D of d^6, and the ^{7}S and the ^{5}S of d^5s.

Obviously, no separate treatment was performed, but in the G.L.S. these few data furnished more points for D′, G, and ζ. Of course, the main role of the G.L.S. in this case was to calculate all the levels of Ru III.

The observed and calculated energy levels are given in table 12.

Rh III – ($4d^7+4d^65s$)

In these configurations theory predicts 33 terms, which split into 82 levels. In AEL all these levels are reported. Only the b^2S of d^6s is considered doubtful.

Even at the preliminary stage of estimating parameters for the first diagonalization we had serious doubts as to the reliability of the experimental material. It is well known that the difference between two terms of d^8s having the same parent term of d^8 is determined by the parameter $G = G_2(4d5s)$. This parameter is very stable for all spectra of the transition elements and also does not change considerably for all spectra of the same sequence. In the present spectrum we could get for the parameter G values which were different from each other by about 1000 cm^{-1}, depending upon the choice of the parent term. Only the difference between (^{5}D)^{4}D and (^{5}D)^{6}D was consistent with the interpolated value of G.

Since the experimental levels did not seem reliable we decided to perform Diag. 1 with interpolated parameters and to use its results for a more detailed critique of the observed levels. We got a very bad fit. The deviations between the calculated levels and those reported in AEL were frequently more than 10000 cm^{-1}. In order to check if there exists any set of parameters which will give calculated values close to the observed ones we included in the first least-squares calculation ("L.S. 1a") 81 levels. Only the b^2S which is reported as doubtful was excluded. We got a mean error of 3094 cm^{-1}. In L.S. 1b only 33 levels were included. We did not include 42 levels belonging to $4d^65s$. The terms b^2D, a^2F, a^2H of $4d^7$ were also included. The mean error reduced to 273, but B′ and C′ assumed nonreasonable values. In L.S. 1c from the configuration d^6s only the levels of (^{5}D) ^{6}D and (^{5}D) ^{4}D were left. The values of B′ and C′ were frozen and we got a mean error of 235. It should be noted that in L.S. 1c we used 6 free electrostatic parameters and 2 frozen ones for the description of only 7 observed terms. Thus, the separate treatment lost its physical significance and we could not use it for further critique of the remaining reported levels.

In the G.L.S. calculations, it turned out that also the other doublets of $4d^7$ were doubtful. Finally, only 16 levels were included in the calculation: the ^{4}F and ^{4}P of $4d^7$ and the (^{5}D) ^{6}D and (^{5}D) ^{4}D of d^6s.

After these calculations had been finished, we had the opprotunity to discuss the results with A. G. Shenstone and he told us that he had reached similar conclusions by comparing the spectrum of Rh III to the isoelectronic spectrum of Ru II, which he analyzed later.

We hope that the predictions of the G.L.S. will help to revise the analysis of this spectrum.

The parameters of the various stages of the calculation are given in table 3, the levels are given in table 13.

Pd III – ($4d^8 + 4d^75s$)

In these configurations theory predicts 21 terms which split into 47 levels. In AEL 19 terms, splitting into 45 levels, are reported. Only the ^{1}S of $4d^8$ and the high ^{1}D of $4d^75s$ were not observed. The level assigned as b ^{3}D$_1$ is reported in AEL as doubtful. It also deviates by about 700 cm^{-1} from its calculated value, thus we did not include this level in the calculations.

In L.S. 1 the mean error was 157 and in L.S. 2 it reduced to 110. Because of the big distance between the configurations $4d^75s$ and $4d^8$ and the weak interaction between them the parameter H is not stable. Pd III is the only spectrum in the sequence in which the number of experimental levels is sufficient to make also the results of the separate treatment quite reliable.

The estimates of parameters of the various stages of the calculation are given in table 4. The observed and calculated levels are given in table 14.

Ag III – ($4d^9 + 4d^85s$)

These configurations consist of 8 terms which split into 18 levels. In AEL only the ^{2}S of d^8s is not reported, and the ^{4}P$_{1/2}$ of d^8s is doubtful. Since also the deviation of this level from its calculated value is rather big, we excluded it from the calculations.

After performing Diag. 1 we saw that the level ^{2}P$_{3/2}$ deviates by more than 1000 cm^{-1} from its calculated value. In L.S. 1a, where it was included, the mean error was 461. In L.S. 1B, from which it was excluded, the mean error reduced to 112. Hence, we did not include this level in the general least squares.

Not having a sufficient amount of experimental material the parameter H was frozen in L.S. 1a and 1b. After having an interpolation formula for the parameter H we could see that we forced H to assume a value which was much bigger than the correct one. Since in the configuration d^8s the parameters H and α can compensate each other, this also caused an unjustified increase of α.

The estimates of parameters of the various stages of the calculation are reported in table 5, the energy levels—in table 15.

Cd III – ($4d^{10} + 4d^95s$)

These configurations include only three terms which split into 5 levels. All are experimentally known.

There is no sense to perform any separate calculation of this spectrum. By including it in the G.L.S. we got an additional value for each of the parameters D′, G, ζ'.

The observed and calculated levels are given in table 16.

5. The Interpolative Treatment of the Whole Sequence

5.1. General Description of the Procedure

In the general (interpolative) treatment the whole sequence is considered as one system, and the coefficients of the interpolation formulas are given the role of free parameters. We call these coefficients "General Parameters."

The parameters B, B′, C, C′, G, H, and α are represented by linear expressions of the form

$$P(n) = \overline{P} + \Delta P \cdot x, \qquad (3)$$

and the parameters D′, ζ, ζ′ by quadratic expressions of the form

$$P(n)=\overline{P}+\Delta P\cdot x+\Delta_2 P\cdot y, \tag{4}$$

where

$$x=n-6 \tag{5a}$$

and

$$y=x^2-10 \tag{5b}$$

Here n is the total number of electrons in the states $4d$ and $5s$. We consider only the coefficients $\overline{P}$, ΔP, and $\Delta_2 P$ as independent parameters (the "general parameters"). The substitution of x and y for n and n^2 is used in order to get fairly orthogonal parameters.

By fitting the interpolation-formulas to the parameters of the separate treatments we obtain a set of initial general parameters. Using these parameters, we diagonalized the matrices of all spectra of the sequences; this is the "General Diagonalization" ("G. Diag.").

In the "General Least-Squares" ("G.L.S.") the known levels of all the spectra are compared with the results of the General Diagonalization. In this unified least-squares calculation only the general parameters specified in table 6 and the normalization parameters $M(d^n)$ are considered as free parameters.

5.2. The Actual Calculations

As a consequence of the separate treatment which was described in the previous chapter we had for the general treatment only 56 reliable observed terms which split into 130 levels. Because of the relatively small amount of experimental material we were forced to use also the results of Zr III and Ag III (which are not quite reliable) for the calculation of the initial interpolation formulas. For the formulas of D′, ζ, and ζ′ even the information from Y III or Cd III was used.

In the G.L.S. we had 30 free parameters: 22 general parameters and 8 additive parameters $M(d^n)$. 25 of them are electrostatic interaction parameters and 5 are spin-orbit interaction parameters.

A total of 483 levels, belonging to 209 terms, were calculated. The *level mean error* of the G.L.S. is

$$\underline{\Delta_{G.L.S.}=77\ \text{cm}^{-1}},$$

and the *term-mean-error* is

$$\underline{\Delta'_{G.L.S.}=91\ \text{cm}^{-1}}.$$

The general parameters of the G. Diag. and the improved general parameters which were obtained in the G.L.S. are given in table 6.

6. Conclusions

We shall use the results in order to evaluate the relative importance of the various improvements to the Slater approximation used in the present paper. Generally speaking an interaction (or a correction-term) is important if, relative to other sequences of the transition elements [1-3] the parameter representing it has a large value and a small relative statistical uncertainty.

We see that the spin-orbit interaction is quite important, and it is certainly the most important correction in the right-hand side of the period. This fact can be seen also from the very mixed assignments given to the levels in tables 7 through 16.

The differences (B′−B), (C′−C), and (ζ′−ζ) are much bigger than the uncertainties of these parameters. This means that it is important to allow these parameters to assume different values for the configurations $4d^n$ and $4d^{n-1}5s$.

The estimates of the parameter α is considerably smaller than in the iron group, but its standard error is much smaller than its value. This means that it is still necessary in order to improve the fit between the theoretical and experimental levels.

Contrary to the results in the first [6] and second [2] spectra of the palladium group, the interaction between the configurations $4d^n$ and $4d^{n-1}5s$ is rather unimportant in the right hand side of the present sequence. This fact manifests itself in the large standard errors of H and the small values it assumes.

Out of 10 spectra of the sequence there are 8 in which the amount of experimental material is not sufficient for a reliable separate treatment. Thus, in this sequence the interpolative method is not only the more reliable one — practically it is the only method which enables us to predict the energy-levels for all the third spectra of the palladium group. We hope that these predictions will help in their experimental observation.

7. Tables of Results* Part A: Parameters

TABLE 1. *Parameters of* Zr III − ($4d^2+4d5s$)

	Diag. 1	L.S. 1*	G.L.S.
A	4840	4807±3	4741
S′	16560	16481±3	16593
B	530	525±0.3	532
C	1600	1829±2	1757
G	3000	2350±3	2454
H	400	fixed	376
α	25	23±0.4	34
ζ	450	410±1.4	411
ζ′	450	454±2.4	461
Δ	....	4	....

*In tables 1-6 the number following the ± sign in the L.S. standard error of the parameter estimate.

Table 2. *Parameters of* Nb III — $(4d^3+4d^25s)$

	Diag. 1	L.S. 1	G.L.S.
A	9260	9308 ± 26	9224
S'	25650	26330 ± 52	26485
B	550	563 ± 2	559
B'	550	593 ± 2	592
C	2200	2054 ± 10	2018
C'	2200	2188 ± 16	2210
G	2400	2386 ± 19	2424
H	400	383 ± 7	334
α	0	30 ± 1	33
ζ	560	544 ± 11	535
ζ'	560	589 ± 11	597
Δ	....	34	....

Table 3. *Parameters of* Rh III — $(4d^7+4d^65s)$

	Diag. 1	L.S. 1a	L.S. 1b	L.S. 1c	G.L.S.
A	11650	12717 ± 1790	11792 ± 1560	11621 ± 146	11895
S'	56750	62083 ± 2454	70184 ± 1570	57185 ± 222	56964
B	669	801 ± 104	651 ± 14	647 ± 21	667
B'	713	980 ± 52	1336 ± 74	fixed	716
C	3068	3616 ± 547	3288 ± 57	3293 ± 56	3062
C'	3194	3844 ± 290	2926 ± 76	fixed	3178
G	2296	2316 ± 297	2276 ± 35	2304 ± 33	2304
H	....	....	....	....	166
α	28	fixed	fixed	24 ± 17	29
ζ	1324	1110 ± 677	1146 ± 64	1141 ± 60	1291
ζ'	1450	1673 ± 490	1395 ± 78	1381 ± 102	1401
n	....	81	33	22	16
Δ	....	3094	273	235	....

n = number of levels included in the L. S. calculations.

Table 4. *Parameters of* Pd III — $(4d+5s)^8$

	Diag. 1	L.S. 1	Diag. 2	L.S. 2	G.L.S.
A	8100	7613 ± 105	7600	7602 ± 90	7663
S'	65100	65836 ± 159	65836	65827 ± 121	65818
B	800	699 ± 13	699	695 ± 9	694
B'	800	747 ± 5	747	744 ± 3	747
C	2500	3221 ± 92	3221	3322 ± 67	3328
C'	3100	3429 ± 25	3429	3445 ± 18	3420
G	2270	2277 ± 24	2277	2274 ± 18	2274
H	385	146 ± 56	235	30 ± 70	124
α	40	31 ± 4	31	28 ± 3	28
ζ	1300	1664 ± 72	1664	1519 ± 43	1545
ζ'	1530	1681 ± 26	1681	1666 ± 18	1667
Δ	....	157	....	110	....

Table 5. *Parameters of* Ag III — $(4d+5s)^9$

	Diag. 1	L.S. 1a	L.S. 1b	G.L.S.
A	1840	1595 ± 400	1689 ± 93	1655
S'	75290	75465 ± 480	75037 ± 115	75125
B'	770	841 ± 33	804 ± 8	778
C'	3210	3063 ± 319	3377 ± 78	3662
G	2270	2413 ± 127	2236 ± 33	2244
H	400	fixed	fixed	82
α	20	68 ± 37	50 ± 9	27
ζ	1730	1846 ± 261	1846 ± 61	1825
ζ'	1730	2031 ± 162	1978 ± 38	1959
Δ	....	461	112	....

Table 6. *General parameters in the third spectra of the palladium-group*

	C. Diag.	G.L.S.
$\bar{D}'$	48792	48746 ± 34
$\Delta D'$	8657	8666 ± 10
$\Delta_2 D'$	85	98 ± 5
$\bar{B}$	640	640 ± 4
ΔB	28	27 ± 1
$\bar{B}'$	691	685 ± 2
$\Delta B'$	34	31 ± 1
$\bar{C}$	2756.9	2803 ± 23
ΔC	232.4	262 ± 8
$\bar{C}'$	2939.9	2939 ± 14
$\Delta C'$	250.7	243 ± 6
$\bar{G}$	2318	2334 ± 10
ΔG	−24	−31 ± 6
$\bar{H}$	250	208 ± 24
ΔH	−40	−42 ± 6
$\bar{\alpha}$	30	31 ± 2
$\Delta\alpha$	0	−0.9 ± 0.7
$\bar{\zeta}$	1190	1193 ± 16
$\Delta\zeta$	221	215 ± 6
$\bar{\zeta}'$	1293	1291 ± 12
$\Delta\zeta'$	232	227 ± 4
$\Delta_2\zeta = \Delta_2\zeta'$	15.5	13 ± 2
Level mean error	....	77
Term mean error	....	91

Tables of Results Part B: Energy Levels

Table 7. *Observed and calculated levels of* Y III

Conf.	Term	*J*	Observed	G.L.S.	
				Calc.	O − C
4*d*	a^2D	3/2	0.0	18	−18
		5/2	724.8	802	−77
5*s*	a^2S	1/2	7466.2	7371	95

TABLE 8. *Observed and calculated levels of Zr* III

Conf.	Term	*J*	Observed	G.L.S.	
				Calc.	O−C
d^2	a^3F	2	0.00	−1	1
		3	681.0	683	−2
		4	1486.4	1488	−2
d^2	a^1D	2	5741.55	5725	16
d^2	a^3P	0	8062.07	8045	17
		1	8325.65	8312	13
		2	8838.21	8833	5
d^2	a^1G	4	11048.70	11067	−18
ds	$(^2D)a^3D$	1	18398.87	18382	17
		2	18802.79	18796	7
		3	19533.35	19532	1
d^2	^1S	0	(13832.0?)	24518	
ds	$(^2D)b^1D$	2	25066.25	25122	−56

TABLE 9. *Observed and calculated levels of Nb* III

Iglesias	Conf.	Term	*J*	Observed	G.L.S.		Calc. g
					Calc.	O−C	
	d^3	a^4F	3/2	0.0	63	−63	0.403
			5/2	515.8	565	−49	1.029
			7/2	1176.6	1208	−32	1.237
			9/2	1939.0	1949	−10	1.331
	d^3	a^4P	1/2	8664.3	8614	50	2.430
			3/2	8607.5	8562	45	1.629
			5/2	9593.7	9486	108	1.596
	d^3	a^2G	7/2	9236.1	9215	21	0.890
			9/2	9804.5	9761	44	1.098
	d^3	^2P	1/2		10753		0.904
a^2D		$^2P+^4P+^2D$	3/2	10912.2	10959	−46	1.307
	d^3	a^2H	9/2	12916.4	12856	60	0.925
			11/2	13263.8	13183	81	1.091
	d^3	$^2D+^2P$	3/2		12894		0.928
		^2D	5/2	13094.0	13041	53	1.203
	d^3	a^2F	7/2	19861.0	19907	−46	1.142
			5/2	19975.0	20061	−86	0.857
	d^2s	$(^3F)b^4F$	3/2	25220.2	25248	−28	0.403
			5/2	25735.2	25759	−23	1.029
			7/2	26463.7	26481	−18	1.238
			9/2	27373.5	27382	−9	1.333
	d^3	^2D	5/2		31463		1.197
			3/2		31785		0.800
	d^2s	$(^3F)b^2F$	5/2	33658.0	33650	8	0.894
			7/2	35079.2	35060	19	1.141
	d^2s	$(^3P)b^4P$	1/2	34514.5	34500	15	2.664
			3/2	34807.2	34797	10	1.704
		$^4P+^2D$	5/2	34989.8	34983	7	1.507
	d^2s	$(^1D)b^2D$	3/2	36535.7	36577	−42	0.832
		$^2D+^4P$	5/2	37114.7	37105	10	1.258
	d^2s	$(^1G)b^2G$	9/2	40875.2	40939	−64	1.112
			7/2	40943.9	40959	−15	0.891
	d^2s	$(^3P)^2P$	1/2		43004		0.672
			3/2		43729		1.328
	d^2s	$(^1S)^2S$	1/2		57154		1.997

TABLE 10. *Observed and calculated levels of Mo* III

Conf.	Term	*J*	Observed	G.L.S.		Calc. g
				Calc.	O−C	
d^4	^5D	0	(0.00)	40	(−40)	
		1	(243.10)	275	(−32)	1.500
		2	(669.60)	688	(−18)	1.499
		3	(1225.20)	1224	(1)	1.498
		4	(1873.80)	1847	(27)	1.497
d^4	^3P	0	(11271.30)	11328	(−57)	
		1	(12509.80)	12554	(−44)	1.493
		2	(14357.30)	14373	(−16)	1.491
d^4	^3H	4	(12630.31)	12634	(−4)	0.843
		5	(13201.34)	13201	(0)	1.043
		6	(13741.54)	13701	(41)	1.167
d^4	^3F	2	(13927.76)	13923	(5)	0.675
	$^3F+^3G$	3	(13947.40)	13924	(23)	1.015
	$^3F+^3G+^3H$	4	(14295.85)	14233	(63)	1.185
d^4	$^3G+^3F$	3	(15672.25)	15835	(−163)	0.822
		4	(16143.15)	16224	(−81)	1.067
	^3G	5	(16763.14)	16629	(134)	1.190
d^4	^3D	3	(19390.90)	19391	(0)	1.329
		2	19783.28	19493	290	1.160
		1	(19995.50)	19806	(190)	0.509
d^4	^1I	6		19754		1.003
d^4	^1G	4		20377		1.008
d^4	^1S	0		22555		
d^4	^1D	2		23221		1.011
d^4	^1F	3		26903		1.005
d^4	^3P	2	(30992.50)	31086	(−93)	1.495
		1	(32292.70)	32323	(−30)	1.493
		0	(32887.80)	32976	(−88)	
d^4	^3F	4	(31932.50)	31970	(−37)	1.245
		3	(32142.80)	32252	(−109)	1.082
		2	(32126.50)	32112	(15)	0.672
d^3s	$(^4F)^5F$	1	(32419.44)	32439	(−20)	0.010
		2	(32844.04)	32854	(−10)	1.000
		3	(33453.10)	33459	(−6)	1.249
		4	(34226.01)	34227	(−1)	1.349
		5	(35130.10)	35122	(8)	1.398
d^4	^1G	4		36033		1.005
d^3s	$(^4P)^5P$	1	(42405.50)	42389	(17)	2.473
	$^5P+^3F$	2	(42665.90)	42652	(14)	1.378
	^5P	3	(43462.69)	43420	(43)	1.596
d^3s	$(^4F)^3F+^5P$	2	(42605.84)	42526	(80)	1.112
	$(^4F)^3F$	3	(43562.61)	43557	(6)	1.142
		4	(44656.23)	44646	(10)	1.231
d^3s	$(^2G)^3G$	3		46227		0.763
		4	(46557.96)	46544	(14)	1.053
		5	(46581.03)	46921	(−340)	1.185
d^4	^1D	2		47541		1.007
d^3s	$(^2P)^3P$	0		48707		
	$^3P+^3D$	1	(48753.45)	48636	(117)	1.159
		2	(49052.05)	48972	(80)	1.383
d^3s	$(^2H)^3H$	4		49460		0.835
		5		50272		1.048
		6		50459		1.167

TABLE 10. *Observed and calculated levels of* Mo III—Continued

Conf.	Term	J	Observed	G.L.S. Calc.	G.L.S. O−C	Calc. g
d^3s	$^3D+^3P+^1P$	1		50200		0.946
	$^3D+^3P$	2		51289		1.284
	^3D	3		51204		1.333
d^3s	$(^2G)^1G$	4		52519		0.985
d^3s	$(^4P)^3P$	0		53082		
	$^3P+^1P+^3D$	1		52528		1.284
	$(^4P)^3P$	2		53858		1.487
d^3s	$(^2H)^1H$	5		54931		1.002
d^3s	$^1P+^3P$	1		55174		1.133
d^3s	$(a^2D)^1D$	2		56633		1.001
d^3s	$(^2F)^3F$	4		58811		1.249
		3		58960		1.084
		2		59121		0.672
d^4	^1S	0		61910		
d^3s	$(^2F)^1F$	3		64072		1.004
d^3s	$(b^2D)^3D$	3		71596		1.329
		2		71793		1.165
		1		71940		0.500
d^3s	$(b^2D)^1D$	2		76887		1.000

TABLE 11. *Calculated levels of* Tc III

Conf.	Term	J	G.L.S.	Calc. g
d^5	^6S	5/2	−2	1.997
d^5	^4G	5/2	19179	0.586
		7/2	19343	0.988
		9/2	19442	1.172
		11/2	19398	1.271
d^5	$^4P+^4D$	5/2	20987	1.510
		3/2	21308	1.564
		1/2	21759	2.207
d^5	^4D	7/2	23007	1.422
	$^4D+^4P$	5/2	23849	1.430
		3/2	23850	1.354
		1/2	23502	0.456
d^5	^2I	11/2	28153	0.933
		13/2	28521	1.077
d^5	$^2D+^2F$	5/2	29536	1.075
	$^2D+^4F$	3/2	30299	0.681
d^5	$^4F+^2G$	9/2	31308	1.292
	$^4F+^2F$	7/2	31291	1.182
	^4F	5/2	31746	1.015
	$^4F+^2D$	3/2	32463	0.534
d^5	$^2F+^4F$	7/2	32182	1.171
	$^2F+^2D$	5/2	33789	1.002
d^5	$^2H+^2G+^4F$	9/2	33612	1.028

TABLE 11. *Calculated Levels of* Tc III—Continued

Conf.	Term	J	G.L.S.	Calc. g
	^2H	11/2	34954	1.083
d^5	^2G	7/2	34555	0.915
	$^2G+^2H$	9/2	35662	1.034
d^5	^2F	7/2	36640	1.146
		5/2	36655	0.872
d^5	^2S	1/2	39605	1.997
d^5	^2D	3/2	44478	0.801
		5/2	44737	1.193
d^4s	$(^5D)^6D$	1/2	44705	3.322
		3/2	45063	1.864
		5/2	45607	1.656
		7/2	46287	1.585
		9/2	47069	1.553
d^5	^2G	9/2	49288	1.111
		7/2	49405	0.891
d^4s	$(^5D)^4D$	1/2	56604	0.053
		3/2	57168	1.206
		5/2	57959	1.367
		7/2	58847	1.427
d^5	^2P	3/2	58686	1.317
		1/2	58938	0.660
d^4s	$(a^3P)^4P$	1/2	61309	2.613
		3/2	62857	1.716
		5/2	65015	1.584
d^4s	$(^3H)^4H$	7/2	61772	0.670
		9/2	62063	1.001
		11/2	62579	1.141
		13/2	63139	1.228
d^4s	$(a^3F)^4F$	3/2	63738	0.419
	$(a^3F)^4F+^4G$	5/2	63609	0.928
		7/2	63808	1.156
		9/2	64055	1.278
d^5	^2D	5/2	64334	1.195
		3/2	64525	0.805
d^4s	$(^3G)^4G+^4F$	5/2	65388	0.692
		7/2	66037	1.041
		9/2	66416	1.188
	$(^3G)^4G$	11/2	66569	1.259
d^4s	$(a^3P)^2P+^4D$	1/2	68826	0.564
	$(a^3P)^2P$	3/2	71968	1.309
d^4s	$(^3H)^2H$	9/2	69062	0.933
	$^2H+^2I$	11/2	69934	1.071
d^4s	$(^3D)^4D$	7/2	69731	1.420
		5/2	69916	1.356
		3/2	69973	1.206
	$^4D+^2P$	1/2	70649	0.170
d^4s	$(a^3F)^2F$	7/2	70791	1.066
d^4s		5/2	71320	0.882
	$(^1I)^2I$	13/2	72399	1.079
	$^2I+^2H$	11/2	72703	0.949
d^4s	$(^3G)^2G$	7/2	72503	0.899
	$(^3G)^2G+(^1G)^2G$	9/2	73239	1.112
d^4s	$(^1G)^2G+(^3G)^2G$	9/2	74267	1.098
	$^2G+^2F$	7/2	74648	0.966
d^4s	$(a^1S)^2S$	1/2	76572	1.966
d^4s	$(^1D)^2D+(^3D)^2D$	3/2	76635	0.807
		5/2	77879	1.197
d^4s	$(^3D)^2D+(^1D)^2D$	5/2	77018	1.187
		3/2	78766	0.809
d^4s	$(^1F)^2F$	7/2	81046	1.153
		5/2	81264	0.891

TABLE 11. *Calculated levels of* Tc III – Continued

Conf.	Term	J	G.L.S.	Calc. g
d^4s	$(b^3P)^4P$	5/2	83340	1.585
		3/2	84675	1.697
		1/2	85616	2.650
d^4s	$(b^3F)^4F$	9/2	84019	1.330
		7/2	84506	1.227
		5/2	84501	1.019
		3/2	84305	0.442
d^4s	$(b^3F)^2F+^2G$	7/2	90827	1.039
	$(b^3F)^2F$	5/2	91454	0.860
d^4s	$(b^3P)^2P$	3/2	91036	1.334
		1/2	92733	0.678
d^4s	$(b^1G)^2G$	9/2	91658	1.113
	$^2G+^2F$	7/2	92142	0.993
d^4s	$(b^1D)^2D$	3/2	104753	0.800
		5/2	104764	1.200
d^4s	$(b^1S)^2S$	1/2	120665	1.999

TABLE 12. *Observed and calculated levels of* Ru III

Conf.	Term	J	Observed	G.L.S. Calc.	G.L.S. O–C	Calc. g
d^6	a^5D	4	0.0	−35	35	1.496
		3	1158.8	1139	20	1.498
		2	1826.3	1827	−1	1.498
		1	2266.3	2279	−12	1.498
		0	2476.0	2495	−19	
d^6	$^3H+^3F+^3G$	4		15028		0.994
	$^3H+^3G$	5		15326		1.066
	^3H	6		15081		1.162
d^6	^3P	2		15092		1.486
		1		18412		1.454
		0		19048		
d^6	$^3F+^3H$	4		16824		1.043
	$^3F+^3G$	3		16857		1.025
	^3F	2		17357		0.677
d^6	$^3G+^3H$	5		18612		1.167
	$^3G+^3F$	4		19611		1.062
		3		19878		0.814
d^6	^3D	1		22495		0.550
		2		22319		1.171
		3		22644		1.328
d^6	^1I	6		23289		1.004
d^6	^1G	4		24503		1.006
d^5s	$(^6S)a^7S$	3	27162.8	27177	−14	1.997
d^6	^1S	0		27242		
d^6	^1D	2		28412		1.008
d^6	^1F	3		31296		1.007
d^6	^3P	0		34942		
		1		35818		1.498
		2		38006		1.491
d^6	^3F	4		36927		1.244
		3		37559		1.079
		2		37008		0.671

TABLE 12. *Observed and calculated levels of* Ru III – Continued

Conf.	Term	J	Observed	G.L.S. Calc.	G.L.S. O–C	Calc. g
d^5s	$(^6S)a^5S$	2	41111.7	41121	−9	1.992
d^6	^1G	4		42394		1.005
d^5s	$(^4G)^5G$	2		51433		0.345
		3		51551		0.924
		4		51674		1.152
		5		51743		1.266
		6		51703		1.332
d^5s	$(^4P)^5P+^5D$	3		53614		1.600
		2		53937		1.701
		1		54432		2.257
d^6	^1D	2		54879		1.013
d^5s	$(^4D)^5D$	4		55985		1.493
	$^5D+^5P$	3		57107		1.542
		2		57152		1.600
		1		56727		1.726
	^5D	0		56198		
d^5s	$(^4G)^3G$	3		60682		0.771
		4		60980		1.054
		5		60957		1.195
d^5s	$(^4P)^3P+^3D$	2		62624		1.323
		1		63453		1.033
	^3P	0		64541		
d^5s	$(^2I)^3I$	5		64001		0.847
		6		64093		1.030
		7		64422		1.143
d^5s	$(^4D)^3D+^3F$	3		65012		1.294
	^3D	2		66051		1.152
	$^3D+^3P$	1		66262		0.669
d^5s	$(^4F)^5F+^5P$	1		65273		0.316
	^5F	2		65408		1.054
	$^5F+^5D$	3		65724		1.275
	^5F	4		65554		1.336
		5		65454		1.382
d^5s	$^3D+^3F+^5F$	3		66565		1.216
	$^3D+^3F+^1D$	2		69516		1.006
	$^3D+^3F+^3P$	1		68811		0.497
d^5s	$^3F+^3D+^3P$	2		67522		0.984
	$^3F+^3G+^3D$	3		70165		1.040
	^3F	4		68919		1.241
d^5s	$(^2I)^1I+^3H$	6		68535		1.002
d^5s	$^3H+^3G$	4		70311		0.923
		5		72693		1.110
	$^3H+^1I$	6		72408		1.139
d^5s	$^3G+^3H$	5		70511		1.126
		4		72228		0.965
	$^3G+^3F$	3		71472		0.908
d^6	^1S	0		71104		
d^5s	$(a^2D)^1D+^3F$	2		73602		0.892
d^5s	$(^2F)^3F$	2		73625		0.705
	$^3F+^1F$	3		73412		1.059
		4		73715		1.227

TABLE 12. *Observed and calculated levels of* Ru III – Continued

Conf.	Term	J	Observed	G.L.S.		Calc. g
				Calc.	O – C	
d^5s	$(^4F)^3F+^1G$	4		74832		1.184
	$^3F+^1F$	3		74904		1.063
	^3F	2		76138		0.738
d^5s	$(^2F)^1F+^3F$	3		75145		1.050
d^5s	$(^2H)^1H$	5		76539		1.008
d^5s	$(^2G)^1G+^3F$	4		77177		1.071
d^5s	$(^2S)^3S$	1		77522		1.997
d^5s	$(^2F)^1F$	3		78799		1.027
d^5s	$(^2S)^1S$	0		82821		
d^5s	$(b^2D)^3D$	1		82910		0.502
		2		83073		1.161
		3		83477		1.311
d^5s	$(b^2D)^1D$	2		87968		0.999
d^5s	$(^2G)^3G$	5		88207		1.200
		4		88335		1.051
		3		88434		0.754
d^5s	$(^2G)^1G$	4		92963		1.001
d^5s	$(^2P)^3P$	2		99093		1.490
		1		99316		1.486
		0		99513		
d^5s	$(^2P)^1P+^3D$	1		103479		0.923
d^5s	$(c^2D)^3D$	3		105494		1.333
		2		105701		1.172
		1		106119		0.595
d^5s	$(c^2D)^1D$	2		110249		1.003

TABLE 13. *Observed and calculated levels of* Rh III

Conf.	Term	J	Observed	G.L.S.		Calc. g
				Calc.	O–C	
d^7	a^4F	9/2	0.0	−25	25	1.327
		7/2	2147.8	2124	24	1.236
		5/2	3485.7	3476	9	1.031
		3/2	4322.0	4328	−6	0.414
d^7—	a^4P	5/2	11062.3	11060	2	1.592
	$^4P+^2P$	3/2	10997.1	11085	−88	1.642
		1/2	12469.8	12519	−50	2.507
d^7	^2G	9/2		13092		1.093
		7/2		15229		0:893
d^7	$^2P+^2D+^4P$	3/2		16334		1.250
	$^2P+^4P$	1/2		18451		0.827
d^7	^2H	11/2		17317		1.091
		9/2		19500		0.931
d^7	^2D	5/2		18436		1.203
	$^2D+^2P$	3/2		21873		0.960
d^7	^2F	5/2		26798		0.863
		7/2		27889		1.140
d^7	^2D	3/2		42251		0.800
		5/2		43173		1.196
d^6s	$(^5D)a^6D$	9/2	43022.0	43010	12	1.552
		7/2	44394.4	44385	9	1.584
		5/2	45278.2	45274	4	1.654
		3/2	45876.6	45876	1	1.862
		1/2	46227.1	46230	−3	3.317

TABLE 13. *Observed and calculated levels of* Rh III – Continued

Conf.	Term	J	Observed	G.L.S.		Calc. g
				Calc.	O–C	
d^6s	$(^5D)a^4D$	7/2	54632.2	54576	56	1.418
		5/2	56125.7	56109	17	1.370
		3/2	57012.5	57013	0	1.200
		1/2	57531.3	57545	−14	0.023
d^6s	$(^3H)^4H$	13/2		62412		1.227
	$^4H+^4G$	11/2		62573		1.153
	$^4H+^4G+^4F$	9/2		62416		1.091
		7/2		62857		0.796
d^6s	$(a^3P)^4P$	5/2		62555		1.585
		3/2		65466		1.574
		1/2		67426		2.523
d^6s	$^4F+^4H$	9/2		64224		1.191
		7/2		64732		1.081
	$^4F+^4G$	5/2		64864		0.957
	$(^3F)^4F$	3/2		65263		0.492
d^6s	$^4G+^4H$	11/2		66126		1.236
	$^4G+^4F$	9/2		67620		1.175
		7/2		68041		1.020
		5/2		67796		0.668
d^6s	$(^3H)^2H$	11/2		69678		1.091
	$^2H+^2G$	9/2		69710		0.964
d^6s	$^2F+^2G+^4D$	7/2		70567		1.123
	$(^3F)^2F$	5/2		72351		0.871
d^6s	$^2P+^4D+^4P$	3/2		70583		1.345
	$^2P+^2S$	1/2		73950		0.842
d^6s	$(^3D)^4D$	1/2		70819		0.159
	$^4D+^2P$	3/2		71264		1.236
	^4D	5/2		70984		1.361
		7/2		71445		1.363
d^6s	$(^3G)^2G$	9/2		73708		1.089
		7/2		74718		0.909
d^6s	$(^1I)^2I$	13/2		74084		1.080
		11/2		74354		0.939
d^6s	$(a^1G)^2G$	9/2		76094		1.096
	$^2G+^2F$	7/2		76404		0.945
d^6s	(3D)^2D	3/2		77596		0.821
		5/2		77834		1.191
d^6s	$^2S+^2P+^4P$	1/2		79502		1.847
d^6s	$(a^1D)^2D$	5/2		80313		1.204
		3/2		80439		0.810
d^6s	$(^1F)^2F$	7/2		82984		1.157
		5/2		83130		0.886
d^6s	$(b^3P)^4P$	1/2		85311		2.601
		3/2		86279		1.718
		5/2		88927		1.579
d^6s	$(b^3F)^4F$	9/2		87320		1.328
		7/2		88264		1.221
		5/2		88099		1.013
		3/2		87453		0.412
d^6s	$(a^3P)^2P$	1/2		92424		0.687
		3/2		95311		1.330
d^6s	$^2F+^2G$	7/2		94021		1.093
	$(b^3F)^2F$	5/2		94542		0.862
d^6s	$(b^1G)^2G$	9/2		95741		1.114
	$^2G+^2F$	7/2		96104		0.940
d^6s	$(b^1D)^2D$	5/2		110016		1.200
		3/2		110018		0.801
d^6s	$(b^1S)^2S$	1/2		128531		1.999

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TABLE 14. *Observed and calculated levels of* Pd III

AEL	Conf.	Term	J	Observed	G.L.S. Calc.	G.L.S. O−C	Calc. g
	d^8	a^3F	4	0.0	2	−2	1.248
			3	3229.7	3227	3	1.083
			2	4687.3	4728	40	0.714
a^1D	d^8	a^3P+^1D	2	10230.5	10330	−99	1.284
		^3P	1	13470.3	13394	76	1.500
			0	13699.1	13636	63	
a^3P_4	d^8	a^1D+^3P	2	14634.3	14768	−133	1.168
	d^8	a^1G	4	17880.4	17824	56	1.002
	d^8	^1S	0		41196		
	d^7s	$(^4F)a^5F$	5	52915.9	52885	31	1.395
			4	55088.8	55040	49	1.344
			3	56741.5	56697	44	1.248
			2	57845.0	57806	39	1.002
			1	58527.3	58492	36	0.017
	d^7s	$(^4F)b^3F$	4	62560.9	62397	163	1.242
			3	65255.4	65181	74	1.151
			2	67079.4	66986	94	0.694
	d^7s	$(^4P)a^5P$	3	65708.0	65689	19	1.595
			2	65788.3	65817	−29	1.754
			1	67151.4	67195	−44	2.403
	d^7s	$(^2G)a^3G$	5	69985.8	70034	−49	1.185
		$^3G+^3H$	4	71047.2	71027	20	1.022
		^3G	3	72786.1	72791	−4	0.759
	d^7s	$(^2P)^3P$	2	72745.0	72859	−113	1.381
		$^3P+^1P+^3D$	1	73002.6	73096	−93	1.259
		$(^2P)^3P+(^4P)^3P$	0	74281.1	74320	−38	
	d^7s	$(^2H)a^3H$	6	74673.3	74741	−67	1.167
			5	75967.6	75971	−4	1.040
		$^3H+^1G$	4	78581.1	78525	56	0.890
	d^7s	$^1G+^3H+^3G$	4	75403.0	75336	67	0.957
	d^7s	$(^4P)c^3P$	2	75455.0	75447	8	1.430
			1	76055.8	76193	−137	1.346
		$(^4P)^3P+(^2P)^3P$	0	78732.5	78682	50	
	d^7s	$(a^2D)a^3D$	3	76231.4	76235	−4	1.331
		$^3D+^1D+^3P$	2	78169.8	78125	45	1.176
		$^3D+^3P+^1P$	1	78120.0	78210	−90	1.049
	d^7s	$(^2H)a^1H$	5	80805.1	80802	3	1.012
	d^7s	$^1P+^3D+^3P$	1	82620.3	82809	−189	0.925
	d^7s	$(a^2D)c^1D+^3P+^3D$	2	83204.3	83113	91	1.074
	d^7s	$(^2F)c^3F$	2	85420.7	85494	−74	0.678
			3	85830.4	85940	−110	1.084
			4	86795.2	86937	−142	1.246
	d^7s	$(^2F)a^1F$	3	90684.3	90857	−173	1.004
	d^7s	$(b^2D)b^3D$	1	(103529.4?)	102858		0.501
			2	103549.6	103296	254	1.160
			3	104419.1	104124	295	1.327
	d^7s	$(b^2D)^1D$	2		108183		1.002

TABLE 15. *Observed and calculated levels of* Ag III

Conf.	Term	J	Observed	G.L.S. Calc.	G.L.S. O−C	Calc. g
d^9	a^2D	5/2	0	23	−23	1.200
		3/2	4607	4587	20	0.800
d^8s	$(^3F)a^4F$	9/2	63250	63283	−33	1.332
		7/2	65764	65744	20	1.226
		5/2	68145	68146	−1	1.031
		3/2	69351	69360	−9	0.440
d^8s	$(^3F)a^2F$	7/2	71691	71579	113	1.151
	$^2F+^2D+^4P$	5/2	73934	73955	−21	1.135
d^8s	$^4P+^2F$	5/2	76406	76415	−9	1.284
	$^4P+^2D$	3/2	77413	77476	−63	1.426
	^4P	1/2	(79326?)	78938		2.656
d^8s	$^2D+^4P+^2P$	3/2	80131	80213	−82	1.189
	$^2D+^4P$	5/2	82231	82363	−132	1.236
d^8s	$^2P+^2D$	3/2	85182	85216	−34	1.212
		1/2	(87477)	85512		0.682
d^8s	$(^1G)a^2G$	9/2	85599	85703	−104	1.113
		7/2	85727	85760	−33	0.893
d^8s	$(^1S)^2S$	1/2		111864		1.994

TABLE 16. *Observed and calculated levels of* Cd III

Conf.	Term	J	Observed	G.L.S. Calc.	G.L.S. O−C	Calc. g
d^{10}	a^1S	0	0.0	−72	72	
d^9s	$(^2D)a^3D$	3	80454.3	80540	−86	1.332
		2	82354.6	82361	−6	1.125
		1	86219.5	86237	−18	0.500
d^9s	$(^2D)a^1D$	2	88871.8	88834	38	1.042

An Additional Remark. The calculations reported in the present paper had been completed about five years ago and then the results were sent to several spectroscopy groups. Some weeks ago, after the stencils for the preprints of this paper had already been typed, we received from Rico a reprint of his paper [7] on the spectrum of Mo III. In table I of his paper he compares his observed levels with our theoretical calculations and the fit is quite good. Checking these results we found out, that by adding to all the calculated levels of Mo III 80 cm^{-1} the fit is very much improved and we get a mean error of 95 cm^{-1} with $M(d^4)$ being the only free parameter. In table 10 we have added the observed levels of Mo III enclosed in brackets in order to indicate that they were not included in the G.L.S.

The author also was informed by L. Iglesias that now she is making a new analysis of Rh III. Hence, we already know that the calculations reported in the present paper actually help in the further analysis of the third spectra of the Pd group.

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