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Fine and hyperfine structure in the atomic spectrum of niobium

Theoretical analysis of the odd configurations and further new levels

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Abstract. A parametric analysis of the fine and the magnetic dipole hyperfine structure for the three configurations of odd parity $4d^3 5s5p$, $4d^4 5p$ and $4d^2 5s^2 5p$ was performed. Effective one-electron parameters were determined and theoretical predictions are given for the magnetic dipole hyperfine structure constants A for the levels of these three configurations. Additionally, 12 new energy levels could be found, four of odd and eight of even parity, by re-analysing data for experimental wavelengths of Nb.

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1 Introduction

The aim of the present work is to extend our systematic studies of the influence of core polarisation effects in magnetic dipole hyperfine structure of transition metals to electron configurations of odd parity. Earlier articles [1–4] have already considered the fine and hyperfine structure of atomic niobium (Nb). The first and the fourth papers [1,4] report on experimental determination of hyperfine structure constants. The first paper [1] includes a comprehensive compilation of all hyperfine structure data known up to 2003. The fourth paper [4] adds magnetic dipole hyperfine structure constants for another 30 fine structure levels. In the second article [2] a parametric analysis of the fine and hyperfine structure is discussed for configurations of even parity. The third article [3] presents experimental investigation of the fine structure in the spectrum of atomic Nb and the discovery of new fine structure levels.

The experimental revision of three known fine structure levels of odd parity and the inclusion of two new levels [3] as well as the expansion of the experimental hyperfine structure data for levels of odd parity leads us to perform a parametric analysis of configurations of odd parity, too.

This parametric analysis raises the question of unknown low lying levels of odd parity. An examination of the comprehensive list of experimental wavelengths from Humphreys and Meggers [5] helps to locate further new fine structure levels, partly included in the fine structure fit.

2 Fine structure

As a prerequisite for the parametric analysis of the hyperfine structure, a parametric study of the fine structure of the odd configurations was performed using the program code RCN, RCG and RCE of Cowan [6]. The calculation has been done in successive SL-coupling. The Moore tables of atomic energy levels [7] are used as experimental basis for the fine structure investigation supplemented by new and revised levels published in [3] and by new levels identified in Section 3 of the present paper. (No data sets for energy levels of the element Nb are available in the NIST atomic spectra database [8].) Following the Moore tables [7] almost all known energy levels of odd parity are assigned to the two configurations $4d^3 5s5p$ and $4d^4 5p$. No assignment is given for some energetically high lying levels. Eight levels close under the ionisation limit are assigned to the configuration $4d^3 5s6p$, and three quartet terms are labeled as the first members of Rydberg series converging to the limit $4d^3(^4\mathrm{F})\,5s\,^3\mathrm{F}$ of Nb II.

In addition to the configurations mentioned above, the configuration $4d^2 5s^2 5p$ is expected to be present in the energy range of the known levels of odd parity. The radial integrals describing the $4d4d$–$4d5s$ and the $4d5p$–$5s5p$

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Table 1. Fine structure parameters for the odd parity configurations $4d^3\,5s5p$, $4d^4\,5p$ and $4d^2\,5s^2\,5p$ of Nb I in cm^{-1} with comparative values from [2] for even parity configurations $4d^4\,5s$, $4d^3\,5s^2$ and $4d^5$.

parameter	1. $4d^3\,5s5p$	2. $4d^4\,5p$	3. $4d^2\,5s^2\,5p$	1. $4d^4\,5s$	2. $4d^3\,5s^2$ [2]	3. $4d^5$
E_{av}	37 120 (100)	40 710 (160)	44 200 (440)	17 170 (60)	12 810 (70)	30 060 (120)
$F^2(4d^2)$	37 010 (550)	33 800 (900)	40 480 c	32 750 (190)	37 400 (300)	29 680 r
$F^4(4d^2)$	20 655 a	18 460 a	23 100 c	19 900 (200)	23 100 (300)	17 140 r
ζ_{4d}	549 f	485 f	613 f	425 (15)	494 (20)	366 r
ζ_{5p}	617 f	411 f	863 f			
$F^1(4d,5p)*$	270 (210)	0 f	0 f			
$F^2(4d,5p)$	10 680 (270)	8 700 (360)	12 370 c			
$G^2(4d,5s)$	11 630 (190)			9 100 (80)		
$G^1(4d,5p)$	5 580 (110)	5 230 (160)	6 010 c			
$G^2(4d,5p)*$	0 f	434 f	0 f			
$G^3(4d,5p)$	1 170 (260)	1 680 b	1 320 c			
$G^1(5s,5p)$	17 500 (350)					
α	21 (6)	21 c	21 c	34 (3)	28 (5)	30 f
β	730 (210)	730 c	730 c			
$R^2(4d5s,4d^2)$	1. – 2.	–13 680 (160)		1. – 3.	–10 700 (600)	
$R^2(5s5p,4d5p)$	1. – 2.	–8 390 d				
$R^1(5s5p,5p4d)$	1. – 2.	–9 280 d				
$R^2(4d^2,4d5s)$	1. – 3.	–13 550 (370)		1. – 2.	–12 600 (300)	
$R^2(4d5p,5s5p)$	1. – 3.	–9 180 e				
$R^1(4d5p,5p5s)$	1. – 3.	–10 150 e				
$R^2(4d^2,5s^2)$	2. – 3.	11 400 e		2. – 3.	10 600 r	
Number of free parameters		17			14	
Number of fitted levels		182			51	
Standard deviation in cm^{-1}		152			70	

* Effective configuration interaction parameter; a: coupled to $F^2(4d^2)$ of the same configuration; b: coupled to $G^1(4d,5p)$ of the same configuration; c: coupled to the same parameter of the configuration 1 ($4d^3 5s5p$); d: coupled to $R^2(4d5s,4d^2)\,(1.-2.)$; e: coupled to $R^2(4d^2,4d5s)\,(1.-3.)$; f: fixed; r: parameter held in a constant ratio with the same parameter in the configurations $4d^4\,5s$ and $4d^3\,5s^2$.

electrostatic interactions are large and therefore the minimum basis set for a significant determination of eigenfunctions in an energy range of 20 000 cm^{-1} above the lowest level $4d^3 5s5p\ ^6G_{3/2}$ is $4d^3 5s5p + 4d^4 5p + 4d^2 5s^2 5p$. The three studied configurations comprise 438 levels, of which 186 are known up to 37 000 cm^{-1} from [3,7] and the present paper.

A total of 45 parameters, listed in Table 1, should be fitted from 186 levels. The most important terms of the effective configuration interaction operators $F_1(4d,5p)$ and $G_2(4d,5p)$ for configurations with several open subshells have been introduced with initial values taken from similar studies in elements close to Nb. In the present case their effect is marginally important.

Due to the neglected configurations which overlap the studied ones beyond 40 000 cm^{-1}, a straight determination of all 45 parameters would lead to meaningless values. Therefore, we introduced a number of additional constraints. Especially for $4d^2 5s^2 5p$, which does not appear as the dominant configuration in the composition of any level, all parameters except the centre of gravity are held in a constant ratio with respect to the corresponding parameters of the configuration $4d^3 5s5p$ using the Hartree-Fock (HF) values as calculated with the RCN subprogram of the Cowan code [6]. Additionally, some of the Slater integrals F, G and R are held in the constant ratio to corresponding parameters (see Tab. 1), also using the HF values.

Since the spin-orbit interaction for Nb is relatively small compared to the electrostatic interaction between the electrons, the contribution of the parameters ζ_{4d} and ζ_{5p} to the fine structure energy is often of the same order of magnitude as the difference between experimental and fitted energies. For this reason, no reliable values could be found for these parameters in a fit of all levels. Therefore, the spin-orbit parameters ζ_{4d} and ζ_{5p} of the configuration $4d^3 5s5p$ were determined from only the levels of the lowest known term of odd parity, the ^{6}G-term, which is almost 100% pure in SL-coupling. From these values, the ζ_{4d} and ζ_{5p} parameters of the other two configurations are calculated using the ratio of the HF values as calculated by the Cowan code [6]. All the spin-orbit parameters remain fixed during the optimization of other parameters.

Finally, convincing results for the fine structure calculations are found with a standard deviation of 152 cm^{-1} using 184 out of 186 experimental levels up

to 37 200 cm^{-1}. The fitted parameters are compiled in Table 1 and compared with the fine structure parameters of the even parity. The corresponding parameters are of comparable magnitude.

The two levels, not taken into account in the fit, are 31 687.53 cm^{-1}, $J = 7/2$ ($g = 1.20$) and 36 511.49 cm^{-1}, $J = 7/2$ (no g given in [7]). In their respective energy ranges, all predicted levels with $J = 7/2$ are known and they are too low to belong to other configurations. For now we consider them as the result of fortuitous wavenumber coincidences. Following the list of experimental wavelength from Humphreys and Meggers [5], the first level is confirmed by four transitions, but two of them are doubly classified, the second level is confirmed by only two transitions.

A comparison between experimental and calculated energies as well as experimental and calculated Landé g-factors is given in Table 2. The energy values show reasonably good agreement. For some levels, especially levels with small J-values, the calculated g-factors deviate widely from the experimental ones. In some cases, there is good agreement between the sum of the two experimental and the two calculated g-factors for two neighbouring levels with strong deviations of the g-factors. This agreement indicates that the real mixing of the wave functions of two close lying levels is weaker or stronger than calculated for these levels. An example for weaker real mixing than calculated are the couples 27 498–27 666 cm^{-1} ($J = 1/2$) and 32 156–32 213 cm^{-1} ($J = 9/2$), where the calculated g values lie in between the two experimental values. Opposite behaviour can be found for example for the couple 26 832–26 896 cm^{-1} ($J = 7/2$), where the real mixing is stronger than the calculated one.

As a result of the fine structure calculations it is found that the coupling conditions are so hopelessly far from any pure-coupling scheme that it is not meaningful to label the energy levels by specification of a term. Nevertheless, in Table 2 the leading component together with the percentage and the configuration of the leading component is given.

The configuration mixing is so strong that an assignment to a particular configuration is meaningless for many levels. To show this, the percentage distribution over the three configurations is listed in column 10 to 12 of Table 2. Especially the contribution of the configuration $4d^2 5s^2 5p$ is dispersed over almost all levels: no single level has a contribution larger than 50% to this configuration (with one exception, a very high lying level at about 53 000 cm^{-1} with $J = 11/2$ and 55% contribution to $4d^2 5s^2 5p$).

Additionally, the results of the calculation show that there are still a few low lying levels of odd parity that have not been identified as yet.

3 New levels

In view of the results of the fine structure calculation, we looked for new energetically low lying levels of odd parity. Using the results of the fine structure calculation for the odd parity and the results from [2] for the even parity, wavelengths and transition probabilities were calculated with the program code of Cowan [6]. Comparing these with the comprehensive list of experimental wavelengths from 300 nm to 1 μm given by Humphreys and Meggers [5] two new levels were found, one at 31 378.58 cm^{-1} with $J = 11/2$, confirmed by six transitions and a second at 35 336.77 cm^{-1} with $J = 13/2$, confirmed by three transitions.

The search for the lowest odd level with $J = 15/2$, belonging to the term $4d^4(^3\mathrm{H})5p\ ^4\mathrm{I}$ is complicated by the fact that it can decay only to $4d^4(^3\mathrm{H})5s\ ^4\mathrm{H}_{13/2}$. However, the consistency of intensities compared to gA transition probabilities and the Zeeman pattern from reference [5] support the classification of the strongest unclassified line ($\lambda = 412.9931$ nm) in the relevant spectral region as $4d^4(^3\mathrm{H})5s\ ^4\mathrm{H}_{13/2}$ at 11 524.65 cm^{-1} to $4d^4(^3\mathrm{H})5p\ ^4\mathrm{I}_{15/2}$ at 35 731.34 cm^{-1}.

Using a level search program written at the Laboratoire Aimé Cotton [9] one further level of odd parity and eight levels of even parity are found. A list of new levels is given in Table 3. The g-factors are determined from the Zeeman patterns measured by Humphreys and Meggers [5]. By using the Zeeman structure type, the known g-factor of the level of opposite parity and the distance between strongest Zeeman components, fairly accurate g-factors (± 0.02) may be obtained although most of the patterns are unresolved and perturbed by the hyperfine structure.

All eight levels of even parity could be assigned to terms of the configurations $4d^4 5s$ and $4d^5$ following the results of the fine structure calculation in [2]. Thus, for the configuration $4d^5$ three levels could be found in addition to the one level previously known.

Additionally, a misprint in the Moore tables for the element Nb [7] is found: the level 35 275.77 cm^{-1} with $J = 11/2$, given in the Moore tables [7], should be at 36 275.77 cm^{-1} as given in the original paper of Humphreys and Meggers [5].

4 Hyperfine structure

The experimental data from the literature [1,4,10–13], which constitutes the basis for the parametric investigations of the magnetic dipole hyperfine structure, is compiled in Table 4. If there is more than one value for an A constant of an energy level, the weighted mean value is used in the fit. Altogether 54 experimental A constants were available for levels of odd parity up to 37 000 cm^{-1}.

According to the effective operator formalism of Sandars and Beck [14], the experimental magnetic dipole hyperfine structure constants A_{exp} of the configurations $4d^3 5s5p$, $4d^4 5p$ and $4d^2 5s^2 5p$ can be expressed as a linear combination of 19 one-electron parameters, three for each of the $4d$ and $5p$ shells of each configuration and one for the $5s$ shell of the configuration $4d^3 5s5p$. The angular coefficients of these parameters have been calculated on the basis of the wave functions from the fine structure calculations using the CHFS program [15]. It should be

Table 2. List of levels of the odd parity configurations $4d^3 5s5p$, $4d^4 5p$ and $4d^2 5s^2 5p$ of Nb I with experimental values $E_{\rm exp}$ and $g_{\rm exp}$ according to [4,7] and Section 3, calculated values $E_{\rm calc}$ and $g_{\rm calc}$ and the respective deviations, leading eigenvector component, percentage distribution over the configurations (1. $4d^3 5s5p$, 2. $4d^4 5p$ and 3. $4d^2 5s^2 5p$) as well as experimental and best fitted hyperfine constants A and the respective deviations. Levels with ΔA in parentheses were excluded from the hyperfine structure fit; energies in $\rm cm^{-1}$; A in MHz. The leading component is given by the intermediate terms in successive SL-coupling; the additional quantum number, given for some intermediate terms of the $4d^n$ subshells, is the Nielson and Koster index.

$E_{\rm exp}$	$E_{\rm calc}$	ΔE	$g_{\rm exp}$	$g_{\rm calc}$	Δg	leading comp.		distr. in %				$A_{\rm exp}$	$A_{\rm calc}$	ΔA
						term		%	1.	2.	3.			
$J = 1/2$														
18 791.09	18 694	97	–0.373	–0.424	0.051	$4d^3 5s5p$	^{4}F ^{5}F ^{6}F	63	87	11	2	–780	–750	30
19 623.96	19 544	80	3.010	2.934	0.076	$4d^3 5s5p$	^{4}F ^{5}F ^{6}D	73	86	13	0		1 509	
20 107.36	20 032	76	–0.020	0.146	–0.166	$4d^3 5s5p$	^{4}F ^{5}F ^{4}D	36	83	13	5		–339	
22 006.74	22 035	–28	2.470	2.467	0.003	$4d^4 5p$	^{5}D ^{4}P	35	30	64	7	–268	–308	–40
23 984.87	23 860	125	–0.601	–0.581	–0.020	$4d^4 5p$	^{5}D ^{6}F	86	10	90	0		1 052	
23 910.90	23 979	–68	2.123	2.127	–0.004	$4d^3 5s5p$	^{2}P ^{3}P ^{2}S	23	37	50	13		498	
25 879.81	25 938	–58	3.220	3.081	0.139	$4d^3 5s5p$	^{4}P ^{5}P ^{6}D	59	78	22	1	1 538	1 033	(–505)
26 717.73	26 370	348	1.141	0.932	0.209	$4d^3 5s5p$	^{4}F ^{3}F ^{4}D	19	42	55	3	508	548	40
26 552.40	26 733	–181	2.441	2.477	–0.036	$4d^4 5p$	^{5}D ^{6}D	40	39	59	2	430	430	0
27 498.94	27 110	389	2.467	2.015	0.452	$4d^4 5p$	^{5}D ^{4}P	19	48	48	4		712	
27 666.46	27 426	240	0.222	0.886	–0.664	$4d^3 5s5p$	^{2}P ^{3}P ^{4}D	18	50	44	6		603	
	28 146			1.801		$4d^3 5s5p$	^{4}P ^{5}P ^{4}P	25	69	25	5		796	
28 442.16	28 444	–2	0.772	1.437	–0.665	$4d^3 5s5p$	^{4}P ^{5}P ^{4}P	16	60	34	6	2 243	2 229	–14
	31 598			0.049		$4d^3 5s5p$	^{2}D$_2$ ^{3}D ^{4}D	50	73	22	5		–575	
32 066.06	32 138	–72	0.046	0.089	–0.043	$4d^3 5s5p$	^{4}P ^{5}P ^{4}D	37	59	22	19		372	
	32 900			0.296		$4d^4 5p$	^{3}P$_2$ ^{4}D	16	58	37	5		519	
33 011.45	33 213	–202	0.460	0.610	–0.150	$4d^3 5s5p$	^{2}D$_2$ ^{3}D ^{2}P	16	71	25	4		319	
33 902.24	33 816	86	0.442	0.981	–0.539	$4d^3 5s5p$	^{2}P ^{1}P ^{2}S	20	75	16	9		691	
34 644.22	34 703	–59	2.050	1.550	0.500	$4d^3 5s5p$	^{2}P ^{1}P ^{2}S	21	75	19	6		1 477	
34 807.57	35 202	–394	2.080	2.416	–0.336	$4d^3 5s5p$	^{2}D$_2$ ^{3}D ^{4}P	34	75	23	2		1 318	
35 920.45	35 782	139	0.019	0.043	–0.024	$4d^4 5p$	^{3}F$_2$ ^{4}D	20	46	41	13		71	
	38 109			0.598		$4d^3 5s5p$	^{2}P ^{1}P ^{2}P	26	45	51	4		916	
	39 395			1.324		$4d^3 5s5p$	^{2}P ^{3}P ^{4}P	12	52	46	1		48	
	39 674			1.216		$4d^3 5s5p$	^{4}F ^{3}F ^{4}D	13	53	46	1		1 306	
$J = 3/2$														
16 672.00	16 653	19	0.000	0.004	–0.004	$4d^3 5s5p$	^{4}F ^{5}F ^{6}G	98	100	0	0	–339	–322	17
19 036.55	18 951	86	1.145	1.126	0.019	$4d^3 5s5p$	^{4}F ^{5}F ^{6}F	67	88	10	1		482	
19 765.18	19 680	85	1.720	1.705	0.015	$4d^3 5s5p$	^{4}F ^{5}F ^{6}D	65	87	12	1		822	
20 383.62	20 359	25	1.260	1.296	–0.036	$4d^3 5s5p$	^{4}F ^{5}F ^{4}D	36	82	13	5		668	
23 006.86	23 055	–48	1.610	1.625	–0.015	$4d^4 5p$	^{5}D ^{4}P	44	31	65	4	–138	–126	12
23 243.87	23 222	22	0.416	0.474	–0.058	$4d^3 5s5p$	^{4}F ^{5}F ^{4}F	49	63	24	13	0	–45	–45
23 525.80	23 849	–323	0.898	0.873	0.025	$4d^3 5s5p$	^{4}F ^{3}F ^{2}D	22	46	47	8	595	556	–39
24 164.79	24 107	58	1.060	1.007	0.053	$4d^4 5p$	^{5}D ^{6}F	70	18	79	3		265	
24 283.34	24 370	–87	2.382	2.373	0.009	$4d^4 5p$	^{5}D ^{6}P	54	43	57	0		492	
25 930.01	25 938	–8	0.467	0.542	–0.075	$4d^4 5p$	^{5}D ^{4}F	33	47	51	2	557	526	–31
26 067.06	26 084	–17	1.820	1.784	0.036	$4d^3 5s5p$	^{4}P ^{5}P ^{6}D	56	76	23	1	944	899	–45
26 713.32	26 677	36	1.450	1.423	0.027	$4d^4 5p$	^{5}D ^{6}D	24	39	57	4	109	299	(190)
26 936.86	26 960	–23	1.292	1.620	–0.328	$4d^4 5p$	^{5}D ^{6}D	40	36	63	2		307	
27 782.57	27 424	359	1.660	1.532	0.128	$4d^4 5p$	^{5}D ^{4}P	20	53	42	6		520	
27 918.85	27 816	103	1.450	1.417	0.033	$4d^4 5p$	^{5}D ^{4}D	18	51	44	6		682	
28 079.09	28 018	61	1.443	1.533	–0.090	$4d^3 5s5p$	^{4}P ^{5}P ^{4}P	21	63	31	6		237	
28 278.25	28 159	119	1.981	2.200	–0.219	$4d^3 5s5p$	^{4}P ^{5}P ^{6}P	45	54	45	1	747	694	–53
28 208.48	28 354	–146	1.794	1.656	0.138	$4d^3 5s5p$	^{4}P ^{5}P ^{4}P	26	71	24	6		926	
29 622.73	29 444	179	0.810	0.811	–0.001	$4d^3 5s5p$	^{4}F ^{3}F ^{2}D	32	76	14	10		142	
29 779.44	29 549	230	0.420	0.441	–0.021	$4d^3 5s5p$	^{2}G ^{3}G ^{4}F	43	72	22	6		60	
31 174.65	31 143	32	1.957	1.950	0.007	$4d^3 5s5p$	^{2}P ^{3}P ^{4}S	42	61	23	17	1 047	1 096	49
31 551.46	31 548	3	0.501	0.565	–0.064	$4d^3 5s5p$	^{2}D$_2$ ^{3}D ^{4}F	29	71	21	8		163	
31 707.94	31 753	–45	0.800	1.041	–0.241	$4d^3 5s5p$	^{2}D$_2$ ^{3}D ^{4}D	41	71	26	4		445	
31 907.74	32 122	–214	0.791	0.697	0.094	$4d^3 5s5p$	^{4}F ^{3}F ^{4}F	19	51	37	12	820	457	(–363)
32 248.69	32 244	5	1.184	1.142	0.042	$4d^3 5s5p$	^{4}P ^{5}P ^{4}D	29	61	23	16		818	
32 623.02	32 618	5	1.000	0.979	0.021	$4d^3 5s5p$	^{4}P ^{3}P ^{2}P	7	58	28	13		709	
33 086.98	33 024	63	1.058	1.045	0.013	$4d^2 5s^2 5p$	^{3}F ^{2}D	9	58	25	17		505	
33 717.01	33 484	233	1.230	1.172	0.058	$4d^4 5p$	^{3}P$_2$ ^{4}D	21	59	34	7		628	
34 252.96	33 785	468		1.536		$4d^3 5s5p$	^{2}D$_2$ ^{3}D ^{2}P	16	70	23	7		867	
34 867.68	34 581	287	1.587	1.767	–0.180	$4d^4 5p$	^{3}P$_2$ ^{4}S	21	63	34	3		625	
34 752.70	34 995	–242	0.948	0.869	0.079	$4d^4 5p$	^{3}P$_2$ ^{2}D	19	53	40	7		418	
35 119.65	35 167	–47	1.806	1.671	0.135	$4d^3 5s5p$	^{2}D$_2$ ^{3}D ^{4}P	40	74	24	2		993	
35 829.46	35 878	–49	0.834	1.122	–0.288	$4d^4 5p$	^{3}F$_2$ ^{4}D	16	44	44	13		700	
36 016.26	35 952	64	1.195	0.888	0.307	$4d^4 5p$	^{3}F$_2$ ^{2}D	18	42	49	9		188	
36 371.05	36 667	–296	1.948	1.969	–0.021	$4d^3 5s5p$	^{4}P ^{5}P ^{4}S	40	59	27	14		781	

Table 2. *Continued.*

$E_{\rm exp}$	$E_{\rm calc}$	ΔE	$g_{\rm exp}$	$g_{\rm calc}$	Δg	leading comp.			distr. in %			$A_{\rm exp}$	$A_{\rm calc}$	ΔA
						term		%	1.	2.	3.			
37 111.67	37 353	–242	0.526	0.658	–0.132	$4d^3 5s5p$	^{2}F ^{3}F ^{4}F	14	64	30	5		113	
	37 892			0.620		$4d^3 5s5p$	^{2}F ^{3}F ^{4}F	15	49	36	14		197	
	38 368			1.257		$4d^3 5s5p$	^{2}P ^{1}P ^{2}P	29	43	52	5		407	
	38 893			0.472		$4d^2 5s^2 5p$	^{3}F ^{4}F	34	28	34	38		318	
	39 399			1.589		$4d^3 5s5p$	^{2}P ^{3}P ^{4}P	15	48	50	2		316	
	39 856			1.318		$4d^3 5s5p$	^{4}F ^{3}F ^{4}D	17	51	47	2		418	
$J = 5/2$														
16 981.01	16 968	13		0.859		$4d^3 5s5p$	^{4}F ^{5}F ^{6}G	99	100	0	0	386	367	–19
19 427.90	19 358	70	1.350	1.336	0.014	$4d^3 5s5p$	^{4}F ^{5}F ^{6}F	75	90	9	1	655	616	–39
19 993.78	19 939	55	1.560	1.587	–0.027	$4d^3 5s5p$	^{4}F ^{5}F ^{6}D	66	88	12	1	827	799	–28
20 837.98	20 858	–20	1.390	1.413	–0.023	$4d^3 5s5p$	^{4}F ^{5}F ^{4}D	40	81	14	5	803	822	19
22 647.03	22 798	–151	0.578	0.580	–0.002	$4d^3 5s5p$	^{4}F ^{5}F ^{4}G	44	84	12	4		74	
23 574.14	23 569	5	1.061	1.070	–0.009	$4d^3 5s5p$	^{4}F ^{5}F ^{4}F	47	63	24	13	516	496	–20
23 684.44	23 754	–70	1.477	1.518	–0.041	$4d^4 5p$	^{5}D ^{4}P	40	31	63	5		140	
24 396.80	24 320	77	1.306	1.307	–0.001	$4d^4 5p$	^{5}D ^{6}F	86	12	88	1	227	206	–21
24 543.13	24 663	–120	1.874	1.869	0.005	$4d^4 5p$	^{5}D ^{6}P	54	42	58	0		286	
24 773.03	25 123	–350	1.300	1.223	0.077	$4d^3 5s5p$	^{4}F ^{3}F ^{2}D	21	48	42	10	170	321	(151)
26 060.65	26 095	–35	1.085	1.103	–0.018	$4d^4 5p$	^{5}D ^{4}F	30	46	51	3	267	333	66
26 386.36	26 371	15	1.610	1.613	–0.003	$4d^3 5s5p$	^{4}P ^{5}P ^{6}D	55	76	23	1	809	855	46
26 983.34	27 122	–139	1.618	1.582	0.036	$4d^4 5p$	^{5}D ^{6}D	56	35	63	2		262	
27 359.70	27 318	42	1.320	1.353	–0.033	$4d^4 5p$	^{5}D ^{4}D	43	42	55	3		219	
27 614.10	27 698	–84	1.370	1.462	–0.092	$4d^3 5s5p$	^{2}P ^{3}P ^{4}P	17	72	21	8		621	
27 797.44	27 933	–135	1.160	1.101	0.059	$4d^3 5s5p$	^{4}F ^{3}F ^{2}F	12	62	22	16		513	
28 445.33	28 183	263	1.606	1.469	0.137	$4d^3 5s5p$	^{4}P ^{5}P ^{4}P	17	65	30	5	608	655	47
28 549.42	28 405	144	1.472	1.531	–0.059	$4d^3 5s5p$	^{4}P ^{5}P ^{4}P	12	57	39	4		695	
28 652.66	28 614	39	1.768	1.822	–0.054	$4d^3 5s5p$	^{4}P ^{5}P ^{6}P	50	58	41	1	746	533	(–213)
29 359.58	29 411	–52	0.693	0.835	–0.142	$4d^3 5s5p$	^{2}G ^{3}G ^{4}G	16	71	19	10		225	
29 775.80	29 690	86	1.348	1.183	0.165	$4d^3 5s5p$	^{4}F ^{3}F ^{2}D	18	76	12	11		617	
29 987.45	29 889	98	1.006	0.891	0.115	$4d^3 5s5p$	^{2}G ^{3}G ^{4}F	31	65	25	10		439	
30 059.60	30 156	–96		1.858		$4d^3 5s5p$	^{4}P ^{5}P ^{6}S	78	95	3	2		1 124	
30 716.50	30 791	–75	0.891	0.876	0.015	$4d^3 5s5p$	^{4}F ^{3}F ^{2}F	26	59	19	22	478	461	–17
31 056.60	30 940	117	0.630	0.655	–0.025	$4d^3 5s5p$	^{4}F ^{3}F ^{4}G	28	59	32	9		560	
31 933.68	31 779	154	0.982	0.763	0.219	$4d^3 5s5p$	^{4}F ^{3}F ^{4}G	14	62	22	16		518	
31 807.55	31 960	–153	1.048	1.171	–0.123	$4d^3 5s5p$	^{2}D$_2$ ^{3}D ^{4}D	34	67	25	8		623	
32 013.40	32 008	5	1.010	1.066	–0.056	$4d^3 5s5p$	^{2}D$_2$ ^{3}D ^{4}F	32	75	22	4		510	
32 139.78	32 178	–39	1.035	0.870	0.165	$4d^3 5s5p$	^{2}G ^{3}G ^{4}G	13	53	30	17		393	
32 545.52	32 517	29	1.320	1.352	–0.032	$4d^3 5s5p$	^{4}P ^{5}P ^{4}D	44	59	18	23		742	
32 654.48	32 681	–26	0.830	0.999	–0.169	$4d^3 5s5p$	^{4}F ^{3}F ^{4}F	22	49	41	9		246	
33 389.87	33 308	82	1.212	1.230	–0.018	$4d^3 5s5p$	^{4}P ^{3}P ^{2}D	13	56	27	17		384	
33 872.18	33 863	10	1.350	1.326	0.024	$4d^4 5p$	^{3}P$_2$ ^{4}D	21	52	38	10		358	
34 654.79	34 641	14	0.627	0.733	–0.106	$4d^3 5s5p$	^{2}H ^{3}H ^{4}G	20	62	34	3		276	
35 099.86	35 053	47	0.868	1.016	–0.148	$4d^3 5s5p$	^{2}D$_2$ ^{3}D ^{4}P	16	61	34	5		412	
34 703.70	35 098	–394	1.550	1.279	0.271	$4d^3 5s5p$	^{2}D$_2$ ^{3}D ^{4}P	29	68	28	4		615	
35 497.48	35 747	–249	1.160	1.178	–0.018	$4d^4 5p$	^{3}P$_2$ ^{2}D	16	54	40	6		530	
36 180.13	35 956	224	1.316	1.232	0.084	$4d^4 5p$	^{3}F$_2$ ^{2}D	15	38	53	9		636	
35 928.35	36 099	–170	1.170	1.217	–0.047	$4d^4 5p$	^{3}F$_2$ ^{4}D	12	50	42	8		468	
36 866.60	36 727	139	0.846	0.961	–0.115	$4d^3 5s5p$	^{4}F ^{3}F ^{2}F	9	57	31	12		374	
37 188.28	37 171	17	0.840	0.886	–0.046	$4d^4 5p$	^{3}G ^{2}F	29	34	60	6		480	
	37 585			1.050		$4d^3 5s5p$	^{2}F ^{3}F ^{4}F	24	60	33	7		423	
	38 021			0.940		$4d^4 5p$	^{3}G ^{4}G	22	40	52	8		399	
	38 347			0.826		$4d^4 5p$	^{3}G ^{4}G	22	35	57	8		397	
	38 781			0.598		$4d^4 5p$	^{3}F$_2$ ^{4}G	25	37	49	14		356	
	39 270			1.043		$4d^2 5s^2 5p$	^{3}F ^{4}F	39	24	36	40		442	
	39 553			1.564		$4d^4 5p$	^{3}D ^{4}P	27	42	57	2		416	
$J = 7/2$														
17 405.32	17 398	7		1.144		$4d^3 5s5p$	^{4}F ^{5}F ^{6}G	99	100	0	0	601	583	–18
19 916.69	19 851	66	1.390	1.399	–0.009	$4d^3 5s5p$	^{4}F ^{5}F ^{6}F	86	92	8	0	681	671	–10
20 315.74	20 336	–20	1.550	1.566	–0.016	$4d^3 5s5p$	^{4}F ^{5}F ^{6}D	75	87	12	1	786	814	28
21 512.18	21 569	–57	1.440	1.440	0.000	$4d^3 5s5p$	^{4}F ^{5}F ^{4}D	48	80	14	6	873	867	–6
23 022.56	23 173	–150	0.980	0.989	–0.009	$4d^3 5s5p$	^{4}F ^{5}F ^{4}G	44	84	12	4	430	464	34
24 015.11	24 051	–36	1.243	1.245	–0.002	$4d^3 5s5p$	^{4}F ^{5}F ^{4}F	47	61	26	12	595	579	–16
24 769.91	24 701	69	1.380	1.389	–0.009	$4d^4 5p$	^{5}D ^{6}F	87	12	87	1		176	
24 904.86	25 041	–136	1.703	1.705	–0.002	$4d^4 5p$	^{5}D ^{6}P	55	43	57	0		418	
26 165.79	26 146	20	1.245	1.259	–0.014	$4d^4 5p$	^{5}D ^{4}F	32	46	54	0	300	328	28

Table 2. *Continued.*

$E_{\rm exp}$	$E_{\rm calc}$	ΔE	$g_{\rm exp}$	$g_{\rm calc}$	Δg	leading comp. term		%	distr. in % 1.	2.	3.	$A_{\rm exp}$	$A_{\rm calc}$	ΔA
26 832.43	26 822	11	1.248	1.493	–0.245	$4d^3 5s5p$	^{4}P ^{5}P ^{6}D	45	69	30	1	378	629	(251)
26 896.68	26 982	–85	1.013	0.774	0.239	$4d^3 5s5p$	^{2}G ^{3}G ^{4}H	57	84	15	1		247	
27 596.74	27 471	126	1.422	1.446	–0.024	$4d^4 5p$	^{5}D ^{4}D	32	39	59	2		115	
27 427.07	27 666	–239	1.567	1.544	0.023	$4d^4 5p$	^{5}D ^{6}D	40	44	55	1	386	369	–17
27 855.13	27 936	–80	0.920	0.893	0.027	$4d^3 5s5p$	^{4}F ^{3}F ^{2}G	33	65	28	7	439	387	–52
28 535.36	28 700	–165	1.120	1.251	–0.131	$4d^3 5s5p$	^{2}P ^{3}P ^{4}D	10	58	27	15	662	620	–42
28 973.12	28 948	25	1.701	1.654	0.047	$4d^3 5s5p$	^{4}P ^{5}P ^{6}P	51	58	40	2		581	
29 209.42	29 131	79	1.241	1.341	–0.100	$4d^3 5s5p$	^{2}P ^{3}P ^{4}D	15	55	36	9	505	522	17
29 271.99	29 343	–71	0.890	0.752	0.138	$4d^3 5s5p$	^{2}H ^{3}H ^{4}H	40	62	37	1	190	173	–17
29 762.70	29 793	–30	0.999	1.071	–0.072	$4d^3 5s5p$	^{2}G ^{3}G ^{4}F	22	68	22	10		476	
30 161.56	30 148	14	1.180	1.103	0.077	$4d^3 5s5p$	^{2}G ^{3}G ^{4}F	22	65	26	9		507	
31 025.52	31 067	–42	1.139	1.127	0.012	$4d^3 5s5p$	^{4}F ^{3}F ^{2}F	98	67	17	16		464	
31 485.20	31 397	88	1.012	1.032	–0.020	$4d^3 5s5p$	^{4}F ^{3}F ^{4}G	21	54	35	11		404	
31 800.74	31 707	94	0.906	0.915	–0.009	$4d^3 5s5p$	^{2}G ^{3}G ^{2}G	29	63	29	8		358	
32 087.58	31 899	189	1.074	1.023	0.051	$4d^4 5p$	^{3}H ^{2}G	14	49	44	8		399	
31 973.24	32 168	–195	1.343	1.304	0.039	$4d^3 5s5p$	^{2}D$_2$ ^{3}D ^{4}D	33	67	31	3		732	
32 451.99	32 322	130	1.115	1.107	0.008	$4d^2 5s^2 5p$	^{3}F ^{4}G	17	61	21	18		604	
32 333.18	32 412	–79	1.199	1.164	0.035	$4d^3 5s5p$	^{2}D$_2$ ^{3}D ^{4}F	18	64	24	12		499	
32 501.33	32 499	2	1.060	1.085	–0.025	$4d^4 5p$	^{3}H ^{2}G	14	58	34	9		348	
33 003.89	32 846	158	1.341	1.411	–0.070	$4d^3 5s5p$	^{4}P ^{5}P ^{4}D	38	63	13	24		712	
32 899.08	33 112	–212	1.170	1.195	–0.025	$4d^3 5s5p$	^{4}F ^{3}F ^{4}F	22	52	42	6		267	
34 319.09	34 019	300	0.870	0.958	–0.088	$4d^3 5s5p$	^{2}G ^{1}G ^{2}G	20	63	22	15		239	
34 168.94	34 210	–41	1.390	1.363	0.027	$4d^4 5p$	^{3}P$_2$ ^{4}D	24	54	38	9		334	
34 853.50	34 793	61	1.000	1.098	–0.098	$4d^3 5s5p$	^{2}H ^{3}H ^{4}G	13	58	38	4		684	
35 178.82	35 179	0	1.117	1.032	0.085	$4d^3 5s5p$	^{2}H ^{3}H ^{4}G	27	54	40	6		436	
36 048.10	36 139	–90	0.925	0.716	0.209	$4d^4 5p$	^{3}G ^{4}H	25	44	54	2		232	
36 334.21	36 216	118	1.378	1.246	0.132	$4d^4 5p$	^{3}F$_2$ ^{4}D	15	52	41	7		572	
36 460.34	36 326	134	0.691	1.030	–0.339	$4d^3 5s5p$	^{2}F ^{1}F ^{2}G	12	56	40	4		408	
36 979.20	36 824	156	1.140	1.154	–0.014	$4d^4 5p$	^{3}G ^{2}F	19	51	41	8		435	
	37 731			1.120		$4d^4 5p$	^{3}G ^{2}F	23	32	64	4		431	
	37 805			1.145		$4d^3 5s5p$	^{2}F ^{3}F ^{4}F	18	46	48	6		438	
	38 163			0.748		$4d^4 5p$	^{3}G ^{4}H	42	17	80	3		436	
	38 471			1.040		$4d^4 5p$	^{3}G ^{4}G	29	32	64	4		388	
	39 022			0.956		$4d^4 5p$	^{3}F$_2$ ^{4}G	21	29	56	15		449	
	39 109			0.919		$4d^2 5s^2 5p$	^{3}F ^{2}G	32	31	34	35		477	
	39 386			0.902		$4d^4 5p$	^{3}G ^{2}G	26	25	71	3		414	
	39 753			1.225		$4d^2 5s^2 5p$	^{3}F ^{4}F	41	19	38	43		479	
$J = 9/2$														
17 937.26	17 933	4		1.273		$4d^3 5s5p$	^{4}F ^{5}F ^{6}G	99	100	0	0	688	674	–14
20 432.11	20 365	67	1.440	1.430	0.010	$4d^3 5s5p$	^{4}F ^{5}F ^{6}F	90	92	8	0		743	
20 733.88	20 853	–119	1.540	1.551	–0.011	$4d^3 5s5p$	^{4}F ^{5}F ^{6}D	82	87	13	0		839	
23 536.77	23 693	–156	1.150	1.176	–0.026	$4d^3 5s5p$	^{4}F ^{5}F ^{4}G	44	85	12	3		618	
24 506.53	24 576	–69	1.336	1.337	–0.001	$4d^3 5s5p$	^{4}F ^{5}F ^{4}F	43	58	31	11	594	622	28
25 199.81	25 135	65	1.427	1.427	0.000	$4d^4 5p$	^{5}D ^{6}F	86	13	86	1		187	
26 440.33	26 415	25	1.334	1.346	–0.012	$4d^4 5p$	^{5}D ^{4}F	27	49	51	1	338	395	57
27 419.62	27 382	37	1.422	1.391	0.031	$4d^3 5s5p$	^{4}P ^{5}P ^{6}D	30	65	34	0	405	492	87
27 331.80	27 485	–153	1.078	1.112	–0.034	$4d^3 5s5p$	^{2}G ^{3}G ^{4}H	52	82	17	0		463	
27 974.87	28 213	–239	1.542	1.526	0.016	$4d^3 5s5p$	^{4}P ^{5}P ^{6}D	52	57	42	1		465	
28 433.74	28 511	–77	1.120	1.142	–0.022	$4d^3 5s5p$	^{4}F ^{3}F ^{2}G	32	57	37	6		312	
29 519.05	29 598	–79	1.010	1.021	–0.011	$4d^3 5s5p$	^{2}H ^{3}H ^{4}H	39	64	35	1		459	
30 117.32	30 060	57	1.276	1.277	–0.001	$4d^3 5s5p$	^{2}G ^{3}G ^{4}F	43	66	29	5		587	
30 279.23	30 396	–116	1.200	1.163	0.037	$4d^3 5s5p$	^{2}G ^{3}G ^{4}G	34	68	22	10		609	
30 940.02	30 853	87	0.88*	0.884		$4d^3 5s5p$	^{2}G ^{1}G ^{2}H	28	83	12	5	0	270	(270)
32 004.63	31 970	35	1.160	1.147	0.013	$4d^3 5s5p$	^{4}F ^{3}F ^{4}G	29	60	38	2		323	
32 156.00	32 051	105	0.835	0.969	–0.134	$4d^3 5s5p$	^{2}H ^{3}H ^{4}I	28	72	26	3		426	
32 213.94	32 146	68	1.092	0.981	0.111	$4d^3 5s5p$	^{2}H ^{3}H ^{4}I	16	64	31	4		377	
32 605.39	32 590	16	1.216	1.160	0.056	$4d^4 5p$	^{3}H ^{2}G	25	47	46	8	265	493	(228)
32 923.87	32 776	148	1.240	1.232	0.008	$4d^3 5s5p$	^{2}D$_2$ ^{3}D ^{4}F	28	65	22	13		609	
32 802.44	32 914	–112	1.210	1.208	0.002	$4d^2 5s^2 5p$	^{3}F ^{4}G	22	57	20	23	617	565	–52
33 136.30	33 513	–377	1.240	1.305	–0.065	$4d^3 5s5p$	^{4}F ^{3}F ^{4}F	24	51	45	5		377	
34 235.04	33 991	244	1.100	1.104	–0.004	$4d^3 5s5p$	^{4}F ^{3}F ^{2}G	23	66	22	12		524	
34 415.52	34 410	6	0.819	0.825	–0.006	$4d^4 5p$	^{3}H ^{4}I	41	30	68	2		426	
35 156.94	35 259	–102	1.073	1.054	0.019	$4d^3 5s5p$	^{2}H ^{3}H ^{4}G	27	50	48	2	633	485	(–148)
35 496.39	35 529	–33	0.954	0.967	–0.013	$4d^4 5p$	^{3}H ^{2}H	26	38	61	1	523	477	–46

Table 2. *Continued.*

$E_{\rm exp}$	$E_{\rm calc}$	ΔE	$g_{\rm exp}$	$g_{\rm calc}$	Δg	leading comp. term		%	distr. in % 1.	2.	3.	$A_{\rm exp}$	$A_{\rm calc}$	ΔA
	35 963			0.938		$4d^3 5s5p$	^{2}H ^{1}H ^{2}H	19	52	46	2		335	
36 333.70	36 404	–70	1.086	0.996	0.090	$4d^4 5p$	^{3}H ^{4}H	23	43	55	2		396	
36 717.11	36 645	72	0.970	1.058	–0.088	$4d^3 5s5p$	^{2}H ^{1}H ^{2}G	16	57	42	1		515	
	37 990			1.256		$4d^4 5p$	^{3}G ^{4}G	18	41	52	6		541	
	38 130			0.979		$4d^4 5p$	^{1}I ^{2}H	20	51	47	2		478	
	38 305			1.124		$4d^4 5p$	^{3}G ^{4}H	19	32	66	2		448	
	38 621			1.036		$4d^4 5p$	^{3}G ^{4}H	26	29	68	3		406	
	39 295			1.096		$4d^4 5p$	^{3}F$_2$ ^{4}G	17	34	51	15		416	
	39 394			1.110		$4d^2 5s^2 5p$	^{3}F ^{2}G	27	26	44	29		442	
	39 709			1.081		$4d^4 5p$	^{3}F$_2$ ^{2}G	15	34	63	4		407	
	39 923			1.020		$4d^4 5p$	^{3}G ^{2}H	25	25	66	9		343	
$J = 11/2$														
18 568.18	18 562	7		1.343		$4d^3 5s5p$	^{4}F ^{5}F ^{6}G	99	100	0	0	727	720	–7
20 939.92	20 893	46		1.448		$4d^3 5s5p$	^{4}F ^{5}F ^{6}F	88	92	8	0	756	821	65
24 203.05	24 370	–167	1.250	1.277	–0.027	$4d^3 5s5p$	^{4}F ^{5}F ^{4}G	44	86	11	3		699	
25 680.36	25 599	82	1.450	1.453	–0.003	$4d^4 5p$	^{5}D ^{6}F	91	8	92	0		149	
	27 961			1.135		$4d^3 5s5p$	^{2}G ^{3}G ^{4}H	68	90	10	0		623	
29 846.50	29 935	–89	1.150	1.143	0.007	$4d^3 5s5p$	^{2}H ^{3}H ^{4}H	44	62	38	0		564	
30 657.60	30 853	–196	1.250	1.260	–0.010	$4d^3 5s5p$	^{2}G ^{3}G ^{4}G	40	70	23	7		666	
31 378.58	31 271	108		1.077		$4d^3 5s5p$	^{2}G ^{1}G ^{2}H	33	84	10	6		684	
32 382.24	32 280	102	0.993	0.994	–0.001	$4d^3 5s5p$	^{2}H ^{3}H ^{4}I	62	74	24	2		386	
32 572.72	32 491	82	1.240	1.264	–0.024	$4d^3 5s5p$	^{4}F ^{3}F ^{4}G	29	58	40	2	0	373	(373)
33 428.20	33 528	–100	1.270	1.265	0.005	$4d^2 5s^2 5p$	^{3}F ^{4}G	32	53	14	33		524	
34 004.08	34 129	–124	0.946	0.947	–0.001	$4d^4 5p$	^{3}H ^{2}I	51	24	75	1		389	
34 838.33	34 855	–17	1.010	1.017	–0.007	$4d^4 5p$	^{3}H ^{4}I	46	29	70	1		387	
35 344.86	35 389	–45	1.140	1.097	0.043	$4d^4 5p$	^{3}H ^{4}I	27	34	65	1		435	
35 630.62	35 638	–7	1.160	1.190	–0.030	$4d^3 5s5p$	^{2}H ^{3}H ^{4}G	25	65	34	0		585	
36 275.77	36 323	–47		1.109		$4d^3 5s5p$	^{2}H ^{3}H ^{2}H	17	45	54	1		547	
36 976.10	36 797	179	1.150	1.128	0.022	$4d^4 5p$	^{3}H ^{4}H	32	39	60	0		455	
	38 005			0.991		$4d^3 5s5p$	^{2}H ^{1}H ^{2}I	41	62	37	1		341	
	38 302			1.199		$4d^4 5p$	^{3}G ^{4}G	41	23	77	0		349	
	38 670			1.111		$4d^4 5p$	^{3}G ^{4}H	32	36	63	1		425	
	38 999			1.136		$4d^4 5p$	^{3}G ^{4}H	23	39	57	3		350	
	39 626			1.190		$4d^4 5p$	^{3}G ^{2}H	16	36	52	13		411	
$J = 13/2$														
19 291.57	19 272	20		1.384		$4d^3 5s5p$	^{4}F ^{5}F ^{6}G	99	100	0	0	739	746	7
	28 503			1.230		$4d^3 5s5p$	^{2}G ^{3}G ^{4}H	69	90	10	0		699	
30 191.25	30 275	–84	1.230	1.229	0.001	$4d^3 5s5p$	^{2}H ^{3}H ^{4}H	48	59	41	0		650	
32 672.39	32 543	130	1.080	1.110	–0.030	$4d^3 5s5p$	^{2}H ^{3}H ^{4}I	78	79	21	0		540	
34 323.20	34 484	–160	1.080	1.079	0.001	$4d^4 5p$	^{3}H ^{2}I	56	25	75	0		448	
35 336.77	35 367	–30	1.15*	1.110	0.04	$4d^4 5p$	^{3}H ^{4}I	77	22	78	0		405	
37 254.41	37 086	168	1.230	1.222	0.008	$4d^4 5p$	^{3}H ^{4}H	38	39	61	0		515	
	38 413			1.082		$4d^3 5s5p$	^{2}H ^{1}H ^{2}I	50	68	32	0		533	
	39 150			1.227		$4d^4 5p$	^{3}G ^{4}H	62	12	88	0		355	
	39 948			0.938		$4d^4 5p$	^{1}I ^{2}K	97	1	99	0		384	
$J = 15/2$														
33 116.36	32 985	131	1.190	1.200	–0.010	$4d^3 5s5p$	^{2}H ^{3}H ^{4}I	80	80	20	0		639	
35 731.34	35 735	–4	1.24*	1.199	0.04	$4d^4 5p$	^{3}H ^{4}I	78	20	80	0		405	

* g-factor determined by re-examination of information given about Zeeman patterns by Humphreys and Meggers [5].

noted that matrix elements of the hyperfine interaction Hamilton operator also occur between different configurations. In general, their contribution to the hyperfine constant A is small. For the configurations of odd parity of Nb, the configuration mixing is very strong and therefore the contribution of these matrix elements may be relevant in some cases. However, taking them into account results in too many fit parameters. Hence these matrix elements between different configurations are not taken into consideration for the fit of the hyperfine structure.

The configuration $4d^2 5s^2 5p$ does not appear as a leading contribution in the composition of any level. To check the percentage distribution over the three highly mixed configurations for the 54 levels with experimentally known A constants, an effective number of levels in all three configurations is estimated by calculating the sum of percentage contributions for all these levels. This gives an effective number of 34.9 levels for the configuration $4d^3 5s5p$, 16.6 levels for $4d^4 5p$ and only 2.5 levels for $4d^2 5s^2 5p$, dispersed over all 54 levels. Therefore it is not possible to fit

Table 3. List of new energy levels of Nb I, found by re-analysing the list of experimental wavelengths from Humphreys and Meggers [5], with g_{exp} deduced from Zeeman data of [5], suggested predominant configuration, calculated energies and calculated g factors following section 2 for the odd parity and following reference [2] for the even parity.

E_{exp}/cm^{-1}	parity	J	g_{exp}	config.	E_{calc}/cm^{-1}	$\Delta E/cm^{-1}$	g_{calc}	Δg	number of classified lines
31 378.58	odd	11/2		$4d^3 5s 5p$	31 271	108	1.077		6
35 336.77	odd	13/2	1.15	$4d^4 5p$	35 367	–30	1.110	0.04	3
35 731.34*	odd	15/2	1.24	$4d^4 5p$	35 735	–4	1.199	0.04	1
40 746.29	odd	11/2	0.97						4
19 034.71	even	7/2	0.92	$4d^4 5s$	18 997	37	0.950	–0.03	12
19 556.91	even	9/2	1.14	$4d^4 5s$	19 530	27	1.110	0.03	10
19 568.72	even	5/2	0.94	$4d^4 5s$	19 461	108	0.920	0.02	11
19 931.98	even	5/2	1.13	$4d^4 5s$	19 840	92	1.142	–0.01	9
20 060.84	even	7/2	1.10	$4d^4 5s$	19 900	161	1.081	0.02	13
22 936.90	even	7/2	0.98	$4d^5$	23 098	–161	0.986	–0.01	7
23 010.58	even	9/2	1.16	$4d^5$	23 137	–126	1.172	–0.01	7
23 048.58	even	11/2	1.25	$4d^5$	23 134	–85	1.272	–0.02	5

* uncertain, because determined with only one line.

Table 4. Experimental magnetic dipole hyperfine structure constants A of the levels of odd parity of Nb I from literature [1,4,11–13]; m: if there are more than one values found in the literature, the weighted mean value is given.

E/cm^{-1}	J	A/MHz		Ref.
18 791.09	1/2	–779.6 (10.0)		[12]
22 006.74	1/2	–267.6 (1.1)	m	[11,13]
25 879.81	1/2	1 537.9 (0.4)		[1]
26 552.40	1/2	430.1 (5)		[11]
26 717.73	1/2	508.3 (4)		[11]
28 442.16	1/2	2 242.7 (1.2)		[11]
16 672.00	3/2	–339.1 (1.0)		[4]
23 006.86	3/2	–137.9 (3)	m	[11,12]
23 243.87	3/2	0 (30)		[4]
23 525.80	3/2	595 (7)		[4]
25 930.01	3/2	557.4 (1)	m	[1,11,12]
26 067.06	3/2	943.5 (1.8)		[12]
26 713.32	3/2	108.6 (4)		[11]
28 278.25	3/2	747.0 (5)	m	[11,13]
31 174.65	3/2	1 047.0 (6.0)		[13]
31 907.74	3/2	820 (60)		[4]
16 981.01	5/2	386 (10)		[4]
19 427.90	5/2	654.7 (10)		[12]
19 993.78	5/2	827 (3)		[4]
20 837.98	5/2	803 (6)		[4]
23 574.14	5/2	515.6 (4)	m	[1,4]
24 396.80	5/2	227 (3)*		[1]
24 773.03	5/2	170.2 (1.9)		[1]
26 060.65	5/2	266.7 (2)	m	[1,11,13]
26 386.36	5/2	809.2 (5)		[11]
28 445.33	5/2	607.8 (6.0)		[13]
28 652.66	5/2	746.2 (6.0)		[13]

E/cm^{-1}	J	A/MHz		Ref.
30 716.50	5/2	477.8 (4)		[11]
17 405.32	7/2	601 (3)		[4]
19 916.69	7/2	680.6 (10.0)		[12]
20 315.74	7/2	786 (5)		[4]
21 512.18	7/2	872.8 (6)	m	[1]
23 022.56	7/2	430 (40)		[4]
24 015.11	7/2	595 (5)		[4]
27 855.13	7/2	439.1 (7)		[4]
26 165.79	7/2	299.6 (10.0)		[12]
26 832.43	7/2	378.4 (8)	m	[1]
27 427.07	7/2	386.0 (5)		[11]
28 535.36	7/2	662 (3)		[1]
29 209.42	7/2	505.4 (6.0)		[13]
29 271.99	7/2	189.5 (3)*		[11]
17 937.26	9/2	687.8 (1.5)		[4]
24 506.53	9/2	594 (3)		[1]
26 440.33	9/2	337.5 (9)	m	[1,11,13]
27 419.62	9/2	405.4 (9)		[1]
30 940.02	9/2	0 (30)		[4]
32 605.39	9/2	264.7 (4.0)		[13]
32 802.44	9/2	617 (8)	m	[4,13]
35 156.94	9/2	632.5 (6.0)		[13]
35 496.39	9/2	522.7 (6.0)		[13]
18 568.18	11/2	726.5 (5)	m	[4]
20 939.92	11/2	756 (4)		[4]
32 572.72	11/2	0 (20)		[4]
19 291.57	13/2	739 (2)		[4]

* typing error in [1].

Table 5. One-electron-parameters of the magnetic dipole hyperfine structure in cm^{-1} for the odd parity configurations $4d^35s5p$, $4d^45p$ and $4d^25s^25p$ of Nb I with comparative values for even parity configurations $4d^45s$, $4d^35s^2$ and $4d^5$ following [2].

	this work			[2]		
	$4d^35s5p$	$4d^45p$	$4d^25s^25p$	$4d^45s$	$4d^35s^2$	$4d^5$
a^{01}_{4d}	476 (19)	408 (44)	533	280 (30)	380 (30)	240
a^{12}_{4d}	1020 (170)	873	1140	210 (100)	250	180
a^{10}_{4d}	342 (68)	–640 (46)	383	–370 (40)	–300 (60)	–650 (60)
a^{10}_{5s}	4520 (160)			6 390 (160)		
a^{01}_{5p}	270 (100)	310 (78)	390			
a^{12}_{5p}	750 (150)	860	1080			
a^{10}_{5p}	650 (160)	960 (110)	940			

the parameters of the latter configuration independently, and all parameters of the $4d$ and $5p$ shell are held at a constant ratio to the corresponding parameter of the configuration $4d^35s5p$ based on the ratio of the fine structure spin-orbit parameters.

In the fit, all levels with a difference between experimental and fitted A constant greater than 100 MHz are excluded. A fit with 13 free parameters results in uncertainties higher than the values themselves for the two parameters a^{12}_{4d} and a^{12}_{5p} of the configuration $4d^45p$. Hence these two parameters are coupled to the parameters a^{01}_{4d} and a^{01}_{5p} of the same configuration using the ratios a^{01}_{4d}/a^{12}_{4d} and a^{01}_{5p}/a^{12}_{5p} from the configuration $4d^35s5p$.

In the final fit with 11 free parameters a standard deviation of 34 MHz is obtained excluding the A constants of 10 levels. The A constants of these 10 levels are excluded due to strong deviations between experimental and calculated A values. A possible reason for these disagreements is the neglecting of the matrix elements of the hyperfine operator between the different configurations. The influence of this neglect may be more considerable in exceptional cases. The calculated and experimental A values as well as their differences are listed in column 13 to 15 of Table 2. The best fitted parameter values are given in Table 5 together with comparative values from the former parametric investigations for the configurations of even parity [2]. The relatively high uncertainties in determination of the one-electron-parameters are due to strong configuration mixing, resulting in uncertainties in the fine structure wave functions, and due to the fact that the p-electron shell contributes with additional parameters.

Just as was observed in the case of even parity, so in the case of odd parity, a strong influence of the core polarization effect is found. This is manifested by the absolute value of the ratio a^{10}_{nl}/a^{01}_{nl} for both the $4d$ and $5p$-electron shell, which is much larger than would be expected from Optimized Hartree-Fock-Slater calculations, done for the even configurations by Olsson and Rosén [16]. Even though the uncertainties in determination of the one-electron-parameters are relatively high, the strong influence of the core polarization is conspicuous.

5 Conclusion and outlook

Continuing our investigation of the core polarization effect in transition metals, we performed a parametric analysis of the fine and hyperfine structure of the odd parity configurations $4d^35s5p$, $4d^45p$ and $4d^25s^25p$ of atomic Nb. The fitted fine structure parameters are in good agreement with parameters found for the even parity configurations of Nb I. Based on experimental hyperfine structure data, greatly extended in recent years, the magnetic dipole hyperfine structure was analysed. The results confirmed the strong influence of the core polarization effect.

In addition to that, 12 new energy levels could be found by re-analysing the comprehensive list of experimental wavelengths from Humphreys and Meggers [5], four of them with odd and eight with even parity. Three levels of odd parity entered in the fine structure calculation.

For the future, further experimental effort is required to resolve open questions concerning the fine and hyperfine structure of atomic Nb. Fourier transform spectroscopy could be used to confirm the new levels by analysing their hyperfine structures and to search for unknown levels which are predicted in the present work and in [2]. Additionally, the amount of experimental data for the magnetic dipole hyperfine structure could be further expanded by measuring and analysing a Fourier transform spectra. Parametric investigation of the electric quadrupole hyperfine structure would give additional information on the quality of the fine structure wave functions, especially concerning the configuration mixing. Up to now this has failed due to lack of sufficient experimental data for the electric quadrupole hyperfine structure. To remedy these deficiencies, experimental investigations are in progress using high resolution spectroscopic methods such as the Doppler-free saturation absorption spectroscopy.

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