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Fine Structure Analysis of the Configuration System of V II. Part II: Odd-Parity Levels

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Abstract

The $3d^34p$, $3d^35p$ and $3d^24s4p$ odd configurations of the V II spectrum have been reanalysed and three $3d^24s4p$ triplets are assigned higher energies than previously proposed. We have determined the fine structure parameters, the largest and next largest eigenvector percentages of levels, their calculated Landé g_J-factors and predicted positions for missing experimental levels up to 100,000 cm^{-1} for the $3d^24s4p$ configuration. Furthermore for the first time a hyperfine structure (HFS) parametric treatment, involving levels of these two configurations has been carried out. The deduced single-electron HFS parameter values are successfully checked with those obtained by means of *ab initio* calculations.

Keywords

Fine Structure, Hyperfine Structure, Energy Levels, *Ab Initio* Calculations, V II Spectrum

1. Introduction

The first analysis of the V II spectrum was done by Meggers and Moore [1] who found most of the predicted terms of the $3d^34p$ configuration and several low terms of the $3d^24s4p$ configuration. Some years later this spectrum was reobserved by the Madrid Group [2] [3] who extended these observations to the vacuum ultraviolet and infrared regions. This permitted to revise the previous assignments and to establish new levels. This V^+ ion fine structure (fs) analysis continued to be improved with the passing years [4]-[7]. Recently we carried out fs studies of some singly ionised atoms, e.g. Ta II [8] or Nb II [9], in an effort to complete previous works and to eliminate erroneous level assignments. This time we propose a similar work concerning V II, which presents high interest for astrophysical investigations since it is very useful in the study of the history of nucleosynthesis, chemically peculiar stars and the sun.

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2. Fine and Hyperfine Structure Analysis

As mentioned in our past work, the complex configuration-interaction between the odd-parity levels, especially between $3d4s^24p$, $3d^24s4p$ and $3d^34p$ of V II, would make this work difficult. To overcome this, we use the extensively tested method of [10]-[12] that is suitable for systems of many mutually interacting Rydberg configurations, with the fs Hamiltonian of [13]-[17]. For this work on V II, we used the following as the configuration basis set: $3d4s^24p$, $3d4s^25p$, $3d^24s4p$, $3d^24s5p$, $3d^34p$, $3d^35p$. Since there are many interaction integrals in this basis, by constraining the radial integrals to physically reasonable ratios [10], which also required a few assumptions from Hartree-Fock calculations, the fit procedure became manageable. Due to the relatively low atomic number of vanadium, LS coupling is preferably used. We fit the odd parity levels, up to 88×10^3 cm^{-1}, that have been observed experimentally [7]. The configurations $3d^24s4p$ and $3d^34p$ have their entire fs parameter set adjusted, while the majority of $3d^35p$ is adjusted. As the levels of the other three configurations are not yet observed experimentally, the fs parameters of states in $3d4s^24p$, $3d4s^25p$ and $3d^24s5p$, that are expected to perturb the states of the three lowest configurations, could not be fit efficiently. Therefore, all parameters in the configurations $3d4s^24p$, $3d4s^25p$ and $3d^24s5p$ are fixed to the weighted values from *ab intio* calculations. Our fs least squares fit of 186 energy levels from [7] used 27 free parameters, for a total of 128 parameters. This fit accurately reproduced the experimental data, with a standard deviation of 70 cm^{-1}, with the exception of three triplets in the $3d^24s4p$ configuration: ^3F, ^1P; ^3D, ^3F, ^1P; ^3F and ^3F, ^1P; ^3G whose level positions should be located higher than given in [7].

In **Table 1**, we show the observed and calculated energy levels, percentages of leading eigenvector components with their LS-term symbols, along with observed and calculated g_J-factors. The fitted fs parameters are listed in **Table 2** and **Table 3** along with, from the Cowan calculations [18], their weighted *ab initio* values. The Slater integral ratio, $0.7959 = \dfrac{F^2(3d,3d)(fs)}{F^2(3d,3d)(ab-initio)} = \dfrac{62803}{78906}$, determined as in [8] [9], for the $3d^24s4p$ configuration, provides the weighting for all parameters except spin-orbit parameters ζ_{nd} and ζ_{np}. Not listed in **Table 2** and **Table 3** are those fs parameters which are fixed to zero as they are theoretically expected to be small. In **Table 4** we propose our predicted positions for the energy levels of these three erroneous triplets. We furthermore present in **Table 4**, for the $3d^24s4p$ configuration, predicted energy level values for all missing experimental values up to 100,000 cm^{-1} to suggest further experimental investigations.

A many-body parametrisation calculation for the HFS analysis allows us to exploit the similarities between configuration interaction effects seen in spin-orbit and hyperfine splitting. Using Equations (4) and (5) in [19] for the A and B HFS constants, the radial parameters $a_{nl}^{\kappa k}$, $b_{nl}^{\kappa k}$, a_i and b_i are determined by fits to experimental values.

The first published magnetic dipole HFS A constants of ^{51}V II, consisting of 24 even levels and 31 odd levels, are determined in 2011 by Armstrong, Rosner and Holt applying fast-ion-beam laser-fluorescence spectroscopy [20], which we use for our HFS fit**.** Our HFS fit does not require us to make extra assumptions for the parameter values as the number of HFS A-values makes the fit overdetermined. We can see from the well-known equation

$$a_{nl}^{\kappa k} = 2\mu_0\mu_B\mu_I \left\langle r^{-3}\right\rangle_{nl}^{\kappa k} \Big/ 4\pi I = 95.4128 g_I \left\langle r^{-3}\right\rangle_{nl}^{\kappa k} \tag{1}$$

(in MHz) that our values for *p*- and *d-electron* HFS many-body parameters are valid; where we use $g_I = \mu_I / I = 5.1485/3.5 = 1.471$ for ^{51}V and show the computed expectation values $\left\langle r^{-3}\right\rangle_{nl}^{\kappa k}$ in **Table 5**.

Previously, it was found [9], even more so for *p-electrons*, that weighting the parameters $a_{nl}^{\kappa k}$ by a ratio of spin-orbit constants obtained thanks to fine structure study and *ab initio* calculations, *i.e.* to multiply the second member of Equation (1) by: $\zeta_{nl}(fs)/\zeta_{nl}(ab\ initio)$ improves the agreement of the calculated HFS values to the experimental values. For *d-electrons* this ratio is generally close to one and is sometimes superfluous to insert it in (1).

To check the value of the most influential HFS-deduced parameter

$$a_{4s}^{10} = 95.4218 g_I \left\langle r^{-3}\right\rangle_{4s}^{10} = 63.6145 g_I 4\pi\left|\psi(0)^2\right| \tag{2}$$

for open *s*-shell configurations which shows that a_{4s}^{10} is directly proportional to *s-electron* density $4\pi\left|\psi(0)^2\right|$

Table 1. Comparison between the observed and calculated energy levels (in·cm^{-1}) and g_J-factors. For each state the parent terms are given immediately after the configuration label in columns 3 & 4.

Obs. energy level [7]	Calc. eigenvalue	Largest eigenvector component (%)	Next largest eigenvector component	Obs g_J [1]	Calc. g_J
J = 0					
37201.35	37253.45	97.68 C ^{4}F; ^{5}D	1.34 C ^{4}P; ^{5}D		0.00
46586.37	46620.65	43.78 C ^{4}P; ^{5}D	43.23 C ^{4}P; ^{3}P		0.00
47027.95	47042.90	55.67 C ^{4}P; ^{5}D	32.80 C ^{4}P; ^{3}P		0.00
48258.22	48424.73	90.02 C ^{2}P; ^{1}S	6.83 C ^{4}P; ^{3}P		0.00
50662.27	50595.02	66.11 C ^{2}P; ^{3}P	25.90 C ^{2}D; ^{3}P		0.00
54813.40	54818.13	40.26 C ^{2}D; ^{3}P	32.62 C ^{2}P; ^{3}P		0.00
65781.80	65853.34	92.75 B ^{3}F, ^{3}P; ^{5}D	4.95 B ^{3}P, ^{3}P; ^{5}D		0.00
75820.80	75761.45	88.60 B ^{3}P, ^{3}P; ^{1}S	7.73 B ^{1}D, ^{3}P; ^{3}P		0.00
76521.80	76607.47	83.94 B ^{1}D, ^{3}P; ^{3}P	7 .73 B ^{3}P, ^{3}P; ^{1}S		0.00
78644.10	78617.11	61.15 C ^{2}D; ^{3}P	16.48 C ^{2}D; ^{3}P		0.00
84875.00	84904.22	83.55 B ^{3}P, ^{3}P; ^{3}P	9.62 C ^{2}D; ^{3}P		0.00
J = 1					
36489.36	36443.81	62.48 C ^{4}F; ^{3}D	30.36 C ^{4}F; ^{5}F	0.35	0.360
36954.63	36926.18	68.43 C ^{4}F; ^{5}F	26.99 C ^{4}F; ^{3}D	0.24	0.166
37259.39	37307.41	94.94 C ^{4}F; ^{5}D	2.46 C ^{4}P; ^{3}D	1.39	1.472
46690.42	46707.50	49.36 C ^{4}P; ^{5}D	40.43 C ^{4}P; ^{3}P	1.44	1.518
46754.59	46753.23	88.99 C ^{4}P; ^{5}P	8.39 C ^{4}P; ^{5}D	2.28	2.398
47107.99	47103.52	43.39 C ^{4}P; ^{3}P	39.12 C ^{4}P; ^{5}D	1.43	1.583
50473.78	50556.41	55.18 C ^{2}P; ^{3}D	23.64 C ^{4}P; ^{3}D	0.49	0.601
50738.76	50692.54	51.56 C ^{2}P; ^{3}P	23.38 C ^{2}D; ^{3}P	1.39	1.401
52181.18	52172.27	81.64 C ^{2}P; ^{3}S	11.01 C ^{4}P; ^{3}S	1.85	1.973
52604.20	52600.72	44.17 C ^{4}P; ^{3}D	16.60 C ^{2}D; ^{1}P	0.63	0.655
52803.75	52800.40	43.79 C ^{2}D; ^{1}P	16.45 C ^{2}D; ^{1}P	0.92	0.876
53751.48	53696.00	61.43 C ^{2}D; ^{3}D	16.94 C ^{2}D; ^{3}D	0.49	0.519
54717.86	54729.40	37.13 C ^{2}D; ^{3}P	30.87 C ^{2}P; ^{3}P		1.503
55663.23	55811.34	71.62 C ^{4}P; ^{3}S	11.01 C ^{2}P; ^{3}S	1.92	1.886
56171.40	56056.95	74.74 C ^{2}P; ^{1}P	9.93 C ^{4}P; ^{3}S	1.05	1.097
63549.20	63498.95	98.42 B ^{3}F, ^{3}P; ^{5}F	1.03 C ^{4}F; ^{5}F		0.000
64930.77	64888.59	86.02 C ^{2}F; ^{3}D	5.48 B ^{3}F, ^{3}P; ^{3}D	0.46	0.499
65815.20	65889.67	92.39 B ^{3}F, ^{3}P; ^{5}D	4.88 B ^{3}P, ^{3}P; ^{5}D		1.496
68759.20	68762.09	76.61 B ^{3}P, ^{3}P; ^{3}D	7.11 B ^{3}P, ^{3}P; ^{3}D		0.502
74723.00	74611.11	91.55 B ^{3}P, ^{3}P; ^{3}S	2.82 C 2P; 3S		1.997
75280.00	75235.89	92.68 B ^{3}P, ^{3}P; ^{5}D	5.21 B ^{2}F; ^{3}P; ^{5}D		1.497

Continued

75716.00	75806.61	60.95 C ^{2}D; ^{3}D	16.80 C ^{2}D; ^{3}D		0.504
76454.70	76455.84	88.52 B ^{1}D, ^{3}P; ^{3}P	3.89 C ^{2}D; ^{3}P		1.500
77555.10	77752.08	69.62 B ^{1}D, ^{3}P; ^{3}D	7.42 C ^{4}F; ^{3}D		0.611
77853.60	77890.67	93.89 B ^{3}P, ^{3}P; ^{5}P	3.67 B ^{1}D, ^{3}P; ^{3}P		2.401
78569.10	78528.32	61.38 C ^{2}D; ^{3}P	16.51 C ^{2}D; ^{3}P		1.493
79259.09	79307.31	55.40 D ^{4}F; ^{3}D	20.23 D ^{4}F; ^{5}D		0.635
82366.50	82402.84	41.03 C ^{2}D; ^{1}P	19.03 B ^{3}P, ^{3}P; ^{1}P		0.884
82497.40	82679.91	56.98 B ^{3}P, ^{3}P; ^{3}D	13.51 C ^{2}D; ^{1}P		0.615
84959.50	84975.66	84.08 B ^{3}P, ^{3}P; ^{3}P	9.38 C ^{2}D; ^{3}P		1.501
J = 2					
34592.75	34560.20	99.41 C ^{4}F; ^{5}G	0.22 D ^{4}F; ^{5}G	0.31	0.333
36673.48	36639.07	60.47 C ^{4}F; ^{5}F	31.55 C ^{4}F; ^{3}D	1.08	1.079
37041.12	37011.05	52.59 C ^{4}F; ^{3}D	38.25 C ^{4}F; ^{5}F	1.08	1.116
37368.96	37409.91	89.41 C ^{4}F; ^{5}D	7.55 C ^{4}F; ^{3}D	1.39	1.473
40001.70	39952.85	94.11 C ^{4}F; ^{3}F	2.55 C ^{2}D; ^{3}F	0.65	0.667
46739.99	46745.10	63.02 C ^{4}P; ^{3}P	17.22 C ^{4}P; ^{5}D	1.48	1.521
46879.88	46871.88	87.48 C ^{4}P; ^{5}P	10.35 C ^{4}P; ^{5}D	1.68	1.794
47101.89	47101.19	69.16 C ^{4}P; ^{5}D	19.27 C ^{4}P; ^{3}P	1.47	1.519
49201.64	49308.81	73.58 C ^{2}G; ^{3}F	10.96 C ^{2}D; ^{3}F	0.63	0.689
49731.24	49798.88	95.20 C ^{4}P; ^{5}S	2.21 B ^{3}P, ^{3}P; ^{5}S		1.983
49898.19	49856.76	47.05 C ^{2}P; ^{1}D	27.56 C ^{2}D; ^{1}D	0.93	1.000
50775.47	50848.26	56.52 C ^{2}P; ^{3}D	28.08 C ^{4}P; ^{3}D	1.11	1.158
51123.21	51070.76	55.95 C ^{2}P; ^{3}P	28.13 C ^{2}D; ^{3}P	1.51	1.496
52245.69	52226.20	57.04 C ^{2}D; ^{3}F	16.95 C ^{2}D; ^{3}F	0.68	0.692
52700.05	52671.60	54.17 C ^{4}P; ^{3}D	26.91 C ^{2}P; ^{3}D	1.10	1.155
53868.61	53822.45	64.72 C ^{2}D; ^{3}D	17.27 C ^{2}D; ^{3}D	1.10	1.170
54715.66	54707.65	37.25 C ^{2}D; ^{3}P	35.10 C ^{2}P; ^{3}P		1.497
57342.56	57227.51	40.78 C ^{2}P; ^{1}D	39.75 C ^{2}D; ^{1}D	0.98	1.002
62084.94	62066.75	78.13 C ^{2}F; ^{3}F	9.36 B ^{3}F, ^{3}P; ^{5}G	0.58	0.637
62285.80	62299.79	89.81 B ^{3}F, ^{3}P; ^{5}G	8.96 C ^{2}F; ^{3}F		0.365
63656.80	63610.68	98.33 B ^{3}F, ^{3}P; ^{5}F	1.02 C ^{4}F; ^{5}F		1.000
64586.14	64567.59	77.95 C ^{2}F; ^{1}D	11.49 C ^{2}D; ^{1}D	1.03	1.000
64804.12	64778.89	85.09 C ^{2}F; ^{3}D	4.98 B ^{3}F, ^{3}P; ^{3}D	1.02	1.165
65884.40	65967.02	91.98 B ^{3}F, ^{3}P; ^{5}D	4.78 B ^{3}P, ^{3}P; ^{5}D		1.497
67737.70	67723.47	79.30 B ^{3}F, ^{3}P; ^{3}F	8.74 C ^{2}F; ^{3}F		0.668
68797.40	68801.51	75.30 B ^{3}F, ^{3}P; ^{3}D	6.89 B ^{3}P, ^{3}P; ^{3}D		1.166

Continued

70923.28	70933.46	78.84 B ^{3}F, ^{3}P; ^{1}D	9.14 B ^{3}P, ^{3}P; ^{1}D		1.002
75401.00	75358.70	90.83 B ^{3}P, ^{3}P; ^{5}D	5 .07 B ^{3}F, ^{3}P; ^{5}D		1.489
75758.20	75826.19	57.76 C ^{2}D; ^{3}D	15.43 C ^{2}D; ^{3}D	1.14	1.147
76220.10	76188.18	76.18 B ^{1}D, ^{3}P; ^{3}F	6.37 B ^{3}F, ^{3}P; ^{3}F		0.703
76252.30	76283.18	88.72 B ^{1}D, ^{3}P; ^{3}P	3.65 C ^{2}D; ^{3}P		1.498
77603.40	77532.67	45.80 C ^{2}D; ^{1}D	17.98 C ^{2}D; ^{1}D		0.937
77640.00	77775.38	29.65 B ^{1}D, ^{3}P; ^{3}D	20.85 B ^{3}P, ^{3}P; ^{5}P		1.160
77857.00	77853.90	31.78 C ^{2}D; ^{3}F	22.75 B ^{1}D, ^{3}P; ^{3}D		0.938
78006.80	78076.34	70.62 B ^{3}P, ^{3}P; ^{5}P	21.31 B ^{1}D, ^{3}P; ^{3}D		1.641
78416.80	78361.81	61.83 C ^{2}D; ^{3}P	16.49 C ^{2}D; ^{3}P		1.494
79435.03	79492.88	61.76 D ^{4}F; ^{3}D	20.82 D ^{4}F; ^{5}D		1.220
79853.58	79943.33	85.50 D ^{4}F; ^{3}F	4.55 B ^{3}F, ^{1}P; ^{3}F		0.676
82593.10	82687.44	75.31 B ^{3}P, ^{3}P; ^{3}D	9.14 B ^{1}D, ^{3}P; ^{3}D		1.167
85102.70	85094.79	76.29 B ^{3}P, ^{3}P; ^{3}P	8.08 C ^{2}D; ^{3}P		1.450
85632.80	85503.49	68.41 B ^{3}P, ^{3}P; ^{1}D	10.04 B ^{3}F, ^{3}P; ^{1}D		1.050
88042.60	87898.97	87.08 B ^{1}G, ^{3}P; ^{3}F	3.64 B ^{3}F, ^{1}P; ^{3}F		0.666
J = 3					
34745.72	34708.47	99.48 C ^{4}F; ^{5}G	0.22 D ^{4}F; ^{5}G	0.93	0.917
36919.21	36912.72	65.56 C ^{4}F; ^{5}F	26.05 C ^{4}F; ^{3}D	1.24	1.287
37204.98	37169.38	48.52 C ^{4}F; ^{3}D	33.15 C ^{4}F; ^{5}F	1.32	1.327
37520.57	37548.06	79.32 C ^{4}F; ^{5}D	16.95 C ^{4}F; ^{3}D	1.47	1.470
39234.05	39281.20	91.32 C ^{4}F; ^{3}G	6.65 C ^{2}G; ^{3}G	0.84	0.752
40195.52	40146.56	93.66 C ^{4}F; ^{3}F	2.48 C ^{2}D; ^{3}F	1.02	1.083
47051.86	47030.91	95.85 C ^{4}P; ^{5}P	3.57 C ^{4}P; ^{5}D	1.55	1.662
47181.18	47176.91	93.19 C ^{4}P; ^{5}D	3.62 C ^{4}P; ^{5}P	1.48	1.506
48579.94	48604.39	81.79 C ^{2}G; ^{3}G	6.54 C ^{4}F; ^{3}G	0.67	0.775
49210.76	49255.07	40.64 C ^{2}G; ^{3}F	36.78 C ^{2}G; ^{1}F	0.99	1.019
49568.42	49558.97	43.22 C ^{2}G; ^{1}F	39.20 C ^{2}G; ^{3}F	0.97	1.040
51085.71	51161.56	53.34 C ^{2}P; ^{3}D	33.43 C ^{4}P; ^{3}D	1.27	1.327
52391.94	52377.75	53.25 C ^{2}D; ^{3}F	15.52 C ^{2}D; ^{3}F	1.07	1.118
52767.30	52704.16	44.10 C ^{4}P; ^{3}D	34.21 C ^{2}P; ^{3}D		1.306
53927.18	53891.67	68.76 C ^{2}D; ^{3}D	17.06 C ^{2}D; ^{3}D	1.37	1.325
55141.98	55143.28	53.24 C ^{2}D; ^{1}F	18.14 C ^{2}H; ^{3}G	0.94	0.959
55349.58	55360.75	73.77 C ^{2}H; ^{3}G	12.59 C ^{2}D; ^{1}F	0.82	0.801
62133.30	62108.43	85.04 C ^{2}F; ^{3}F	8.62 B ^{3}F, ^{3}P; ^{3}F	1.00	1.079
62444.10	62469.11	96.93 B ^{3}F, ^{3}P; ^{5}G	2.31 C ^{2}F; ^{3}F		0.921

Continued

63816.70	63776.74	98.00 B ^{3}F, ^{3}P; ^{5}F	1.02 C ^{4}F; ^{5}F		1.249
64057.54	63966.63	93.42 C ^{2}F; ^{3}G	2.78 C ^{2}H; ^{3}G	0.72	0.754
64603.44	64597.08	86.12 C ^{2}F; ^{3}D	4.46 B ^{3}F, ^{3}P; ^{3}D	1.22	1.331
65995.60	65962.16	91.53 B ^{3}F, ^{3}P; ^{5}D	4.66 B ^{3}F, ^{3}P; ^{5}D		1.496
66303.84	66090.73	72.05 C ^{2}F; ^{1}F	23.31 B ^{3}F, ^{3}P; ^{1}F	0.95	1.005
67904.80	67897.11	78.91 B ^{3}F, ^{3}P; ^{3}F	8.38 C ^{2}F; ^{3}F		1.084
68945.00	68954.00	76.78 B ^{3}F, ^{3}P; ^{3}D	7.08 B ^{3}P, ^{3}P; ^{3}D		1.332
69644.00	69611.72	91.59 B ^{3}F, ^{3}P; ^{3}G	2.43 B ^{1}G, ^{3}P; ^{3}G		0.755
70936.01	71023.39	72.01 B ^{3}F, ^{3}P; ^{1}F	19.78 C ^{2}F; ^{1}F		0.999
75573.90	75531.06	85.88 B ^{3}P, ^{3}P; ^{5}D	4.77 B ^{3}F, ^{3}P; ^{5}D		1.477
75847.90	75897.82	59.41 C ^{2}D; ^{3}D	15.20 C ^{2}D; ^{3}D	1.27	1.334
76385.40	76291.21	74.90 B ^{1}D, ^{3}P; ^{3}F	5.96 B ^{3}F, ^{3}P; ^{3}F		1.108
77686.00	77790.39	47.22 C ^{2}D; ^{3}F	18.07 C ^{2}D; ^{3}F		1.155
77841.90	77871.93	38.48 B ^{1}D, ^{3}P; ^{3}D	30.00 B ^{3}P, ^{3}P; ^{5}P		1.384
78301.00	78398.37	63.18 B ^{3}P, ^{3}P; ^{5}P	29.14 B ^{1}D, ^{3}P; ^{3}D		1.546
79327.56	79412.43	73.04 C ^{2}D; ^{1}F	17.95 C ^{2}D; ^{1}F		1.002
79696.98	79750.85	72.46 D ^{4}F; ^{3}D	12.77 D ^{4}F; ^{5}D		1.347
79881.11	80046.73	90.08 B ^{1}G, ^{3}P; ^{3}G	2.81 B ^{3}F, ^{1}P; ^{3}G		0.750
80057.61	80122.35	61.69 D ^{4}F; ^{3}F	24.84 D ^{4}F; ^{3}G		1.005
80463.03	80253.33	70.86 D ^{4}F; ^{3}G	22.57 D ^{4}F; ^{3}F		0.838
82715.10	82789.09	76.44 B ^{3}P, ^{3}P; ^{3}D	7.64 B ^{3}F, ^{3}P; ^{3}D		1.334
87933.50	87806.42	88.89 B ^{1}G, ^{3}P; ^{3}F	3 .22 B ^{1}D, ^{3}P; ^{3}F		1.083
J = 4					
34946.55	34903.61	99.55 C ^{4}F; ^{5}G	0.22 D ^{4}F; ^{5}G	1.14	1.150
37150.51	37166.50	97.75 C ^{4}F; ^{5}F	0.99 B ^{3}F, ^{3}P; ^{5}F		1.351
37531.08	37596.15	96.63 C ^{4}F; ^{5}D	1.27 C ^{4}P; ^{5}D	1.44	1.499
39403.74	39446.81	91.14 C ^{4}F; ^{3}G	6.53 C ^{2}G; ^{3}G	1.03	1.052
40430.04	40384.04	93.74 C ^{4}F; ^{3}F	2.39 C ^{2}D; ^{3}F	1.22	1.250
47056.32	47093.49	86.49 C ^{2}G; ^{3}H	12.64 C ^{2}H; ^{3}H	0.78	0.801
47420.25	47399.36	97.20 C ^{4}P; ^{5}D	1.35 B ^{3}F, ^{3}P; ^{5}D	2.28	1.501
48730.72	48758.93	87.68 C ^{2}G; ^{3}G	6.70 C ^{4}F; ^{3}G	1.02	1.052
49268.55	49340.63	62.64 C ^{2}G; ^{3}F	25.11 C ^{2}G; ^{1}G	1.18	1.183
49723.61	49759.63	71.93 C ^{2}G; ^{1}G	20.84 C ^{2}G; ^{3}F	0.96	1.061
52082.82	52091.71	85.42 C ^{2}H; ^{3}H	12.62 C ^{2}G; ^{3}H	0.70	0.803
52657.47	52623.38	64.03 C ^{2}D; ^{3}F	18.58 C ^{2}D; ^{3}F	1.18	1.250
54144.17	54126.35	82.69 C ^{2}H; ^{1}G	11.76 C ^{2}F; ^{1}G	1.00	1.001

Continued

55304.30	55337.50	89.90 C ^{2}H; ^{3}G	2.41 C ^{2}F; ^{3}G	1.02	1.049
62176.19	62155.68	87.41 C ^{2}F; ^{3}F	8.20 B ^{3}F, ^{3}P; ^{3}F	1.36	1.249
62682.06	62706.56	98.85 B ^{3}F, ^{3}P; ^{5}G	0.44 C ^{2}F; ^{3}F		1.151
64026.20	63991.68	89.51 B ^{3}F, ^{3}P; ^{5}F	8.38 C ^{2}F; ^{3}G		1.323
64130.80	64051.47	84.92 C ^{2}F; ^{3}G	8.92 B ^{3}F, ^{3}P; ^{5}F	1.02	1.078
65790.18	65865.87	86.11 C ^{2}F; ^{1}G	11.49 C ^{2}H; ^{1}G	0.94	1.000
66157.60	66271.20	92.46 B ^{3}F, ^{3}P; ^{5}D	4.63 B ^{3}P, ^{3}P; ^{5}D		1.499
68147.06	68134.81	80.34 B ^{3}F, ^{3}P; ^{3}F	7.95 C ^{2}F; ^{3}F		1.251
69911.80	69871.78	92.89 B ^{3}F, ^{3}P; ^{3}G	2.55 B ^{1}G, ^{3}P; ^{3}G		1.051
75824.80	75757.49	82.72 B ^{3}P, ^{3}P; ^{5}D	9.13 B ^{1}D, ^{3}P; ^{3}F		1.473
76643.30	76520.70	70.04 B ^{1}D , ^{3}P;^{3}F	10.45 B ^{3}P, ^{3}P; ^{5}D		1.278
77968.90	77925.51	58.96 C ^{2}D; ^{3}F	22.39 C ^{2}D; ^{3}F		1.251
80013.14	80086.00	91.91 B ^{1}G , ^{3}P;^{3}G	2.50 B ^{3}F , ^{3}P; ^{3}G		1.050
80298.06	80355.08	53.56 D ^{4}F; ^{3}F	38.08 D ^{4}F; ^{3}G		1.175
80595.56	80486.10	59.16 D ^{4}F; ^{3}G	34.75 D ^{4}F; ^{3}F		1.129
83962.90	83985.15	99.36 B ^{1}G , ^{3}P; ^{3}H	0.26 C ^{2}H; ^{3}H		0.800
87789.70	87674.31	89.42 B ^{1}G , ^{3}P; ^{3}F	3.29 B ^{1}D , ^{3}P; ^{3}F		1.250
J = 5					
35193.13	35144.52	99.60 C ^{4}F; ^{5}G	0.22 D ^{4}F; ^{5}G	1.16	1.267
37352.45	37375.04	97.92 C ^{4}F; ^{5}F	0.99 B ^{3}F, ^{3}P; ^{5}F	1.40	1.399
39612.96	39657.86	91.10 C ^{4}F; ^{3}G	6.44 C ^{2}G; ^{3}G	1.19	1.202
47297.04	47322.97	85.79 C ^{2}G; ^{3}H	12.98 C ^{2}H; ^{3}H	1.01	1.034
48853.04	48880.09	85.03 C ^{2}G; ^{3}G	6.75 C ^{4}F; ^{3}G	1.22	1.190
49593.36	49581.65	72.03 C ^{2}G; ^{1}H	22.36 C ^{2}H; ^{1}H	0.95	1.008
52153.46	52166.53	86.17 C ^{2}H; ^{3}H	12.99 C ^{2}G; ^{3}H	0.98	1.034
52877.89	52870.87	98.95 C ^{2}H; ^{3}I	0.48 C ^{2}G; ^{1}H	0.84	0.835
55206.79	55117.15	61.02 C ^{2}H; ^{3}G	25.31 C ^{2}H; ^{1}H	1.15	1.133
55499.34	55390.59	49.51 C ^{2}H; ^{1}H	30.86 C ^{2}H; ^{3}G	1.03	1.067
62987.60	63006.78	99.33 B ^{3}F, ^{3}P; ^{5}G	0.38 B ^{3}F, ^{3}P; ^{5}G		1.267
64229.19	64148.53	91.63 C ^{2}F; ^{3}G	3.16 B ^{3}F, ^{3}P; ^{5}F		1.207
64286.60	64270.71	95.39 B ^{3}F, ^{3}P; ^{5}F	3.19 C ^{2}F; ^{3}G		1.394
70227.60	70184.45	93.39 B ^{3}F, ^{3}P; ^{3}G	2.63 B ^{1}G , ^{3}P; ^{3}G		1.201
80155.72	80137.63	92.40 B ^{1}G , ^{3}P; ^{3}G	2.60 B ^{3}F, ^{3}P; ^{3}G		1.200
80767.64	80698.89	97.24 D ^{4}F; ^{3}G	0.61 B ^{3}F, ^{1}P; ^{3}G		1.201
84137.30	84152.34	99.36 B ^{1} G , ^{3}P; ^{3}H	0.26 C ^{2}H; ^{3}H		1.034

Continued

J = 6					
35483.39	35428.86	99.62 C ^{4}F; ^{5}G	0.22 D ^{4}F; ^{5}G		1.334
47607.79	47616.47	86.36 C ^{2}G; ^{3}H	13.19 C ^{2}H; ^{3}H	1.13	1.167
52252.60	52272.52	85.96 C ^{2}H; ^{3}H	13.27 C ^{2}G; ^{3}H	1.04	1.166
53076.71	53067.02	99.45 C ^{2}H; ^{3}I	0.31 C ^{2}H; ^{3}H	0.98	1.024
55403.30	55580.73	99.59 C ^{2}H; ^{1}I	0.23 C ^{2}H; ^{3}H	1.01	1.001
63357.30	63366.75	99.49 B ^{3}F, ^{3}P; ^{5}G	0.38 B ^{3}F, ^{3}P; ^{5}G		1.334
84342.90	84349.18	99.49 B ^{1}G , ^{3}P; ^{3}H	0.26 C ^{2}H; ^{3}H		1.167
J = 7					
53319.56	53305.96	99.84 C ^{2}H; ^{3}I	0.15 D ^{2}H; ^{3}I		1.143

B: $3d^2 4s4p$ configuration; C: $3d^3 4p$ configuration; D: $3d^3 5p$ configuration.

Table 2. Fine structure fitted parameters values (in·cm^{-1}) for the odd-parity levels of V II (Fit) and corresponding weighted *ab initio* values.

Configuration	$3d^1 4s^2 4p^1$	$3d^2 4s^1 4p^1$		$3d^3 4p^1$		$3d^2 4s^1 5p^1$	$3d^3 5p^1$
		F.V.	C.C	F.V.	C.C		
Eav	121463[f]	80,172 (23)		52,332 (15)	50,535	119953[f]	93789 (22)
F^2 (3d, 3d)		62,803 (144)	62,803[a]	56,187 (70)	56,652	63419[f]	57493[f]
F^4 (3d, 3d)		39,639 (227)	39,299	33,419 (159)	35,212	39715[f]	35775[f]
F^2 (3d, np)	14228[f]	16,167 (101)	14,685	11,842 (82)	11,471	3150[f]	3161[f]
G^1 (3d, np)	5002[f]	6011 (110)	4855	5507 (39)	4928	3662[f]	1173[f]
G^3 (3d, np)	4472[f]	3697 (267)	5402	2239 (129)	3961	964[f]	1028[f]
G^1 (4s, np)		34,041 (114)	31,226			1054[f]	
G^2 (3d, 4s)		7694 (217)	11,629			8668[f]	
ζ_{3d}	236[f]	206 (13)	206	168 (10)	176	208[f]	179[f]
ζ_{np}	363[f]	332 (37)	275	259 (23)	204	76[f]	66[f]

F.V.: fitted value; C.C.: Cowan code; [a]: fixed to fitted value; [f]: fixed to weighted *ab initio* value (C.C.).

Table 3. Fitted configuration interaction parameters.

Values of main configuration interaction parameters in·cm^{-1}		
$3d4s^2 4p$ - $3d^2 4s4p$	R^1 (5p5s, 4d5p)	−3359[f]
	R^2 (5s5p, 4d5p)	−3370[f]
$3d4s^2 4p$ - $3d^3 4p$	R^2 (5s5s, 4d4d)	11412[f]
	R^2 (5p5s, 4d5p)	−6048 (371)
$3d^2 4s4p$ - $3d^3 4p$	R^1 (5s5p, 4d5p)	−9559 (208)
	R^2 (4d5s, 4d4d)	−3554 (187)

Table 4. Predicted positions for missing experimental energy levels of the $3d^2 4s4p$ configuration up to 100,000 cm^{-1}, resulting LS-percentage of the largest wave function component and the corresponding calculated Landé g_J-factor.

Configuration	J value	Designation	Energy (cm^{-1})	Composition LS (%)	Calc. g_J
$3d^2 4s4p$					
		^3F, ^1P; ^3D			
	1		89143	56	0.504
	2		89363	55	1.166
	3		89680	53	1.334
		^3F, ^1P; ^3F			
	2		88643	60	0.668
	3		88864	55	1.064
	4		89141	53	1.235
		^3F, ^1P; ^3G			
	3		88548	72	0.771
	4		88809	70	1.065
	5		89152	74	1.200
		^3P, ^3P; ^5D			
	0		75172	93	0.000
		^3P, ^3P; ^1P			
	1		88665	73	0.997
		^3P, ^3P; ^5S			
	2		73804	97	1.998
		^1D, ^3P; ^3P			
	2		76283	89	1.498
		^1D, ^1D; ^1F			
	3		99800	76	1.016
		^3F, ^3P; ^1G			
	4		73589	96	1.001

we suggest to compare the ratio: $a_{4s}^{10}\left(3d^3 4s\right)_{\text{Fit}} \Big/ a_{4s}^{10}\left(3d^2 4s4p\right)_{\text{Fit}} = \dfrac{4519.76}{6014} = 0.7725$ obtained by using fitted experimental HFS V II data (**Table 5** of Part I of this work and **Table 5** of part II) to the same ratio $a_{4s}^{10}\left(3d^3 4s\right)_{ab\ initio} \Big/ a_{4s}^{10}\left(3d^2 4s4p\right)_{ab\ initio} = \dfrac{43.09}{55.77} = 0.7726$ using the computed data given in **Table 6**, obtained thanks to use of the pseudo relativistic Hartree-Fock code [21]. We can see that these two ratios are very similar to the fourth decimal place and we can conclude that the $a_{4s}^{10}\left(3d^2 4s4p\right)_{\text{Fit}}$ value is very satisfactory. In **Table 5**, comparing the *ab initio* and fitted HFS one-electron parameters for *d*-, *p*- and *s-electrons* we have achieved good agreement further verifying the veracity of the fitting model. Moreover we confirm through our calculations the well-founded basis of the experimental data of Armstrong, Rosner and Holt [20], gathered in **Table 7** where one can note that experimental values are close to calculated ones except for the level whose energy is equal to 54718 cm^{-1}.

Table 5. The fitted and calculated main HFS many-body parameters (in MHz). The uncertainties given in parentheses are the standard deviations. Radial integrals are computed by means of the Cowan code.

Configuration	$3d^2 4s4p$	$3d^3 4p$
$\langle r^{-3}\rangle_{4d}$ (a.u.)	3.040	2.646
ζ_{3d} (cm^{-1}) *Ab-initio*	206	176
ζ_{3d} (cm^{-1}) Fit	206.18 (12.79)	167.71 (10.38)
a_{4d}^{01} cal (MHz)	427.04	353.88
a_{4d}^{01} (Fit) (MHz)	426.17 (1.47)	367.36 (1.26)
$\langle r^{-3}\rangle_{np}$ (a.u.)	2.378	1.761
ζ_{4p} (cm^{-1}) *Ab-initio*	275	204
ζ_{4p} (cm^{-1}) Fit	331.79 (37.16)	258.91 (22.72)
a_{4p}^{01} cal (MHz)	402.68	313.69
a_{4p}^{01} (Fit) (MHz)	394.23 (7.30)	292.13
a_{4s}^{10} (Fit) (MHz)	6014 (246)	
a_{4s}^{10} cal (MHz)	5851.14	

Table 6. Pseudo-relativistic Hartree-Fock estimates of $4\pi|\Psi(0)|^2$ (in units of a_0^{-3}) for configurations of interest here, using the PSUHFR code [21].

Configuration	$3d^2 4s^1 4p^1$	$3d^3 4s^1$
1 s	51,903	51,906
2 s	4638	4638
3 s	622	606
4 s	55.77	43.09
Total[a] s-electron density	114,380	114,345

[a]Totals are contribution from all s-orbitals weighted by their occupation numbers.

Table 7. Predicted HFS A constants of ^{51}V II (in MHz), compared with those obtained experimentally by Armstrong, Rosner and Holt [20].

Level (cm^{-1})	J value	A(MHz)$_{Experimental}$ [20]	A(MHz)$_{Calculated}$ This work
36489	1	715.84	701.18
36955	1	827.39	816.95
52604	1	532.12	550.05
52804	1	496.9	490.26
53751	1	432.83	440.04
54718	1	38.93	67.84
55663	1	−317.77	−259.60
36673	2	239.52	238.51
37041	2	300.37	307.70
40002	2	609.63	613.78

Continued

52246	2	520.47	521.79
52700	2	270.37	258.59
53869	2	222.87	232.10
54716	2	131.00	138.93
57343	2	342.90	343.33
37205	3	160.22	177.29
39234	3	501.86	498.12
40196	3	301.13	301.48
49211	3	400.45	425.61
49568	3	326.76	327.53
52392	3	326.62	315.08
52767	3	141.03	128.18
53927	3	233.25	236.59
66304	3	397.45	429.20
37531	4	85.61	98.32
39404	4	304.11	304.40
40430	4	178.23	174.53
52657	4	239.99	227.86
62176	4	351.28 or −276.67	339.91
37352	5	161.02	165.45
39613	5	213.51	216.29

3. Conclusion

We studied the spectrum of V II which permits to point out the incorrect positions of three triplets. We give refined fine structure parameters and leading eigenvectors percentages of levels and for the first time the calculated magnetic Landé g_I-factors, which are very useful for missing level assignments. Taking advantage of recent experimental work on hyperfine structure of this ion [20] we were also able to determine for the first time the predominant single-electron HFS parameter values, confirmed using *ab initio* calculations. It would be interesting to extend this study experimentally to the missing levels of $3d^2 4s4p$ to compare with our predicted positions. Further experimental work on the unknown levels of $3d^3 4p$, $3d^3 5p$, $3d4s^2 4p$, $4d5s^2 5p$ *and* $3d^2 4s5p$ configurations would also be useful, since the situation is already formulated for future investigations of all existing levels of this basis.

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