Calculation of atomic structure of doubly ionized vanadium

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Introduction

Atomic structure and spectroscopic properties of the neutral and ionized vanadium is of great interest to several fields of applied and fundamental science

Practical needs:

- astrophysics
- industrial devices
- plasma physics
- controlled thermonuclear fusion
- laser development

Fundamental problems:

- term-dependence of orbitals
- electronic correlations
- orbital relaxation
- spectroscopic data for weak lines
- new theoretical models

General information

Vanadium:

transitional metal with open d-shell

Z = 23

$V_I: 1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2\ {}^4F$
$E_{ion} = 6.746$ eV

$V_{II}: 1s^2 2s^2 2p^6 3s^2 3p^6 3d^4\ {}^5D$
$E'_{ion} = 14.634$ eV

$V_{III}: 1s^2 2s^2 2p^6 3s^2 3p^6 3d^3\ {}^4F$
$E''_{ion} = 29.311$ eV

Electronic structure

Principal electronic configurations according to LS approximation

In scope of LS-coupling scheme, most observed energy levels of exited states of doubly ionized vanadium V_{III} can be classified as $3d^2(^ML)nl$ configurations based on different ancestral terms (^ML) of V_{IV} ion. Unlike neutral and singly ionized vanadium, for the V_{III} only one term belongs to the "doubly excited" configuration system — $3d4s4p\ {}^4D^o$. Despite this, such complex electronic structure of the atomic system still leads to high number of LS terms.

Table 1. Number of terms for principal electronic configurations of V_{III} states

Configuration	Terms	Number of terms
$3d^3$	$^{2,4}P\ {}^2D\ {}^{2,4}F\ {}^2GH$	8
$3d^2 4s$	$^{2,4}S\ {}^{2,4}P\ {}^2D\ {}^{2,4}F\ {}^2G$	7
$3d^2 4p$	$^{2,4}SPDFG\ {}^2H^o$	19
...		
Total:		120

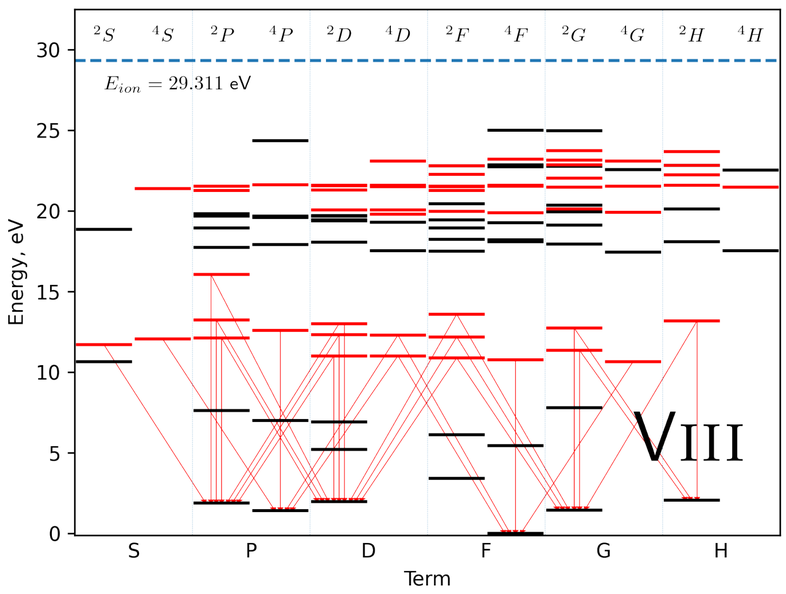

Figure 1. **Energy levels and main transitions.** Energy levels diagram of vanadium ion according to the NIST data [1]. The energies for multiplets are averaged over the fine structure levels. Black dashes correspond to even terms, red dashes — odd terms. Arrows indicate the main allowed transitions between the levels. The levels are grouped according to the total orbital angular momentum L and the multiplicity $2S+1$ of the terms in the LS coupling approximation.

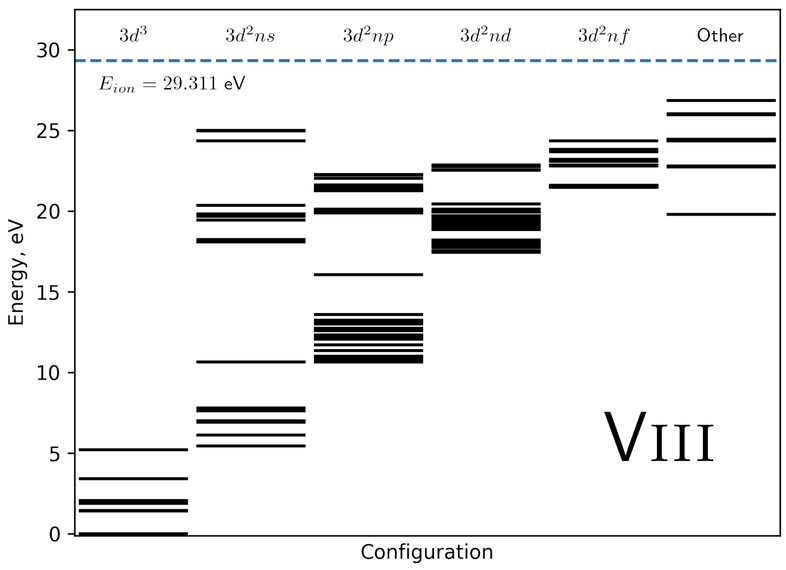

Figure 2. **Energy levels diagram of vanadium ion according to the NIST data [1].** The energies for multiplets are averaged over the fine structure levels. The levels are grouped according to the electronic configuration of the atomic states in the LS coupling approximation.

Theoretical methods

In most cases, the theoretical study of spectroscopic properties requires knowledge of wave functions. Multi-configuration Hartree–Fock (MCHF) method combined with configuration interaction (CI) methods are a method of choice for complex atoms where atomic state functions are expanded in a basis of configuration state functions [2].

Schroedinger equation:

$$H\Psi = E\Psi$$

Multi-configuration expansion:

$$\Psi(\gamma LS) = \sum_i c_i \Phi(\gamma_i LS), \quad \sum_i c_i^2 = 1$$

Ψ — atomic state function (ASF), Φ — configuration state function (CSF)

Configuration interaction method:

$$\mathbf{Hc} = E\mathbf{c}$$

Hamiltonian matrix elements:

$$H_{ij} = \langle \Phi(\gamma_i LS)|H|\Phi(\gamma_j LS)\rangle$$

Hartree–Fock method:

$$\Phi(\gamma LSM_L M_S) = \sum_i c_i \, |u_1^i u_2^i \dots u_N^i\rangle$$

where $|u_1 \dots u_N\rangle$ — Slatter determinants

$$|u_1 \dots u_N\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} \langle t_1|u_1\rangle & \cdots & \langle t_1|u_N\rangle \\ \vdots & \ddots & \vdots \\ \langle t_N|u_1\rangle & \cdots & \langle t_N|u_N\rangle \end{vmatrix}$$

$t = (\mathbf{r}, \sigma)$ — stands for position and spin of the individual electron, and u stands for the one-electron orbital $|u\rangle = |nlm\mu\rangle$

Computational details

To calculate the wave functions of the ground and lower excited states of vanadium ion V_{III} we employed multi-configuration Hartree–Fock method (MCHF) [3] together with configuration interaction (CI) approach with non-orthogonal orbitals and B-splines as basis functions [4, 5]. This approach allows to take into account the term-dependence of valence orbitals, the effects of correlation and relaxation.

Spectroscopic orbitals of **deep core** $1s$, $2s$, and $2p$ were caclulated for the ground state of vanadium ion $V_{III}\ 3d^3\ {}^4F$ using Hartree–Fock (HF) method.

Valence orbitals $3s$, $3p$, $3d$, $4s$ and $4p$ were calculated separately for different configurations. They were obtained from term-average HF-calculations for each of the principal electronic configurations under consideration: $3d^3$, $3d^2 4s$, and $3d^2 4p$.

After that, the spectroscopic orbitals mentioned above were supplemented by sets of correlation orbitals $4l$ and $5l$ ($l = 0$–4). The correlation orbitals were obtained in separate MCHF calculations for one of the terms for each of the selected configurations. Subsequently, the obtained sets of the correlation orbitals were used in the calculations of all other terms with the same configuration. In the calculations of each of the sets of correlation orbitals, one- and two-electron excitations from the outer shells were included in the multi-configuration expansions:

$$\Psi(3dnln'l'\ LS) = \sum_i c_i \Phi(3d\bar{n}l\bar{n}'\bar{l}'\ LS)$$

where $\bar{n}l\bar{n}'\bar{l}'$ denotes all possible one- and two-electron promotions (for both spectroscopic and correlation orbitals)

The configurations with the mixing coefficients less than 0.001 were excluded from the final CI-expansions.

References

[1] Kramida, A., Ralchenko, Yu., Reader, J., and NIST ASD Team (2022). NIST Atomic Spectra Database (ver. 5.10). Available: https://physics.nist.gov/asd

[2] C. Froese Fischer *et al* 2016 J. Phys. B. **49** 182004; doi:10.1088/0953-4075/49/18/182004

[3] C. Froese Fischer *et al* 2007 Comput. Phys. Commun. **176** 8, 559-579; doi:10.1016/j.cpc.2007.01.006

[4] O. Zatsarinny and C. Froese Fischer 2000 Phys. Commun. **124** 2–3, 247-289; doi:10.1016/S0010-4655(99)00441-5

[5] O. Zatsarinny and C. Froese Fischer 2009 Comput. Phys. Commun. **180** 11, 2041–2065; doi:10.1016/j.cpc.2009.06.007

Further improvement

- Additional research for states with $3d^2 4s$ configuration
- Finetune energies using different cut-off parameters for CI-expansions
- Quasi-relativistic CI-calculations with Breit–Pauli Hamiltonian and J-dependent ASF

$$H_{BP} = H_{NR} + H_{RS} + H_{FS}$$

$$\Psi^{\beta J\pi} = \sum_{\alpha LS} C(\beta J\pi; \alpha LS\pi)\Phi^{\alpha LS\pi}$$

$\Phi^{\alpha LS\pi}$ — multiconfigurational expansions from the LS calculations

$C(\beta J\pi; \alpha LS\pi)$ — spin-orbit mixing of different LS terms

Results

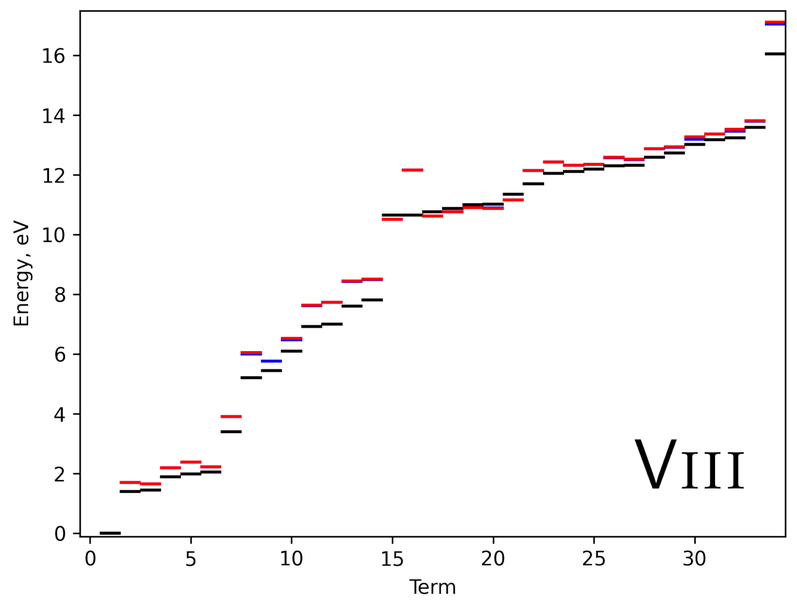

Figure 3. **Comparison of excitation energies.** Black dashes — experimental energies [1];blue dashes — present calculations, full CI-expansion; red dashes — present calculations, CI-expansion with the mixing coefficients > 0.001.

Table 2. Excitation energies of the lower states of vanadium ion.

N	Config.	Term	E_{ex} NIST, eV	E_{ex} MCHF, eV	ΔE_{ex}, eV	N_{conf}
1	$3d^3$	a ^4F	0.000	0.000		32 (61)
2	$3d^3$	a ^4P	1.405	1.708	0.304	26 (44)
3	$3d^3$	a ^2G	1.457	1.662	0.205	54 (111)
4	$3d^3$	a ^2P	1.887	2.200	0.312	50 (78)
5	$3d^3$	a $^2D2$	1.986	2.381	0.395	70 (126)
6	$3d^3$	a ^2H	2.054	2.220	0.167	41 (73)
7	$3d^3$	a ^2F	3.402	3.916	0.514	64 (116)
8	$3d^3$	b $^2D1$	5.204	6.051	0.847	70 (126)
9	$3d^2[^3F]4s$	b ^4F	5.456			– (61)
10	$3d^2[^3F]4s$	b ^2F	6.108	6.526	0.418	45 (116)
...						
32	$3d^2[^3P]4p$	y $^2P^o$	13.241	13.525	0.284	69 (92)
33	$3d^2[^1G]4p$	x $^2F^o$	13.596	13.806	0.211	84 (128)
34	$3d^2[^1S]4p$	x $^2P^o$	16.051	17.114	1.063	69 (92)

Table 3. Dependence of the deviation of the excitation energies on the number of configurations included in the CI-expansion.

Config.		MCHF			**MCHF 0.001**			MCHF 0.01		
		ΔE_{ex}, eV	$\frac{\Delta E_{ex}}{E_{NIST}}$, %	N_{conf}	ΔE_{ex}, eV	$\frac{\Delta E_{ex}}{E_{NIST}}$, %	N_{conf}	ΔE_{ex}, eV	$\frac{\Delta E_{ex}}{E_{NIST}}$, %	N_{conf}
$3d^3$	min	0.166	8	44	0.167	8	26	0.148	7	8
	median	0.312	15	111	0.312	16	54	0.336	20	13
	max	0.796	22	126	0.847	22	70	1.083	24	15
$3d^2 4s$	min	0.307	6	38	0.418	7	17	0.375	6	7
	median	0.695	10	78	0.726	10	40	0.688	10	13
	max	1.503	14	126	1.504	14	56	1.428	13	18
$3d^2 4p$	min	0.103	1	14	0.103	1	10	0.128	1	4
	median	0.193	2	92	0.209	2	69	0.229	2	13
	max	1.002	6	128	1.063	7	84	1.277	8	18
Total	min	0.103	1	14	0.103	1	10	0.128	1	4
	median	0.279	3	92	0.285	3	52	0.336	3	13
	max	1.503	22	128	1.504	22	84	1.428	24	18

Table 4. Correlation configurations and their mixing coefficients for the primary configurations of vanadium ion.

Primary config.	Correlation config.	Mixing coeff.	Primary config.	Correlation config.	Mixing coeff.
$3d^3$	$3d5d^2$	-0.047	$3d^2 4p$	$3d4s4f$	0.035
	$3d5d^2$	0.031		$3d4d5p$	0.031
	$3d^2 5d$	-0.019		$3d^2 5p$	0.028
	$3d4d5d$	0.016		$3d4d4f$	-0.021
	$3d^2 5d$	0.013		$3d4p4d$	-0.01
	$3d^2 4d$	0.012		$3d4p5g$	-0.01
	$3d5p^2$	-0.012		$3d^2 4f$	0.009
	$3d^2 5g$	0.009		$3d4d4f$	0.008
	$3d4d^2$	-0.008		$3d^2 4f$	0.008
	$3d4d5d$	-0.007		$3d4d5p$	0.008
	$3d^2 4d$	-0.007		$3d^2 5f$	-0.008
	$3d4d^2$	0.006		$3d^2 5f$	-0.007
	$3d5g^2$	0.006		$3d4p5g$	-0.007
	$3d5g^2$	-0.006		$3d4p5d$	0.006
	$3d4f5p$	0.005		$3d5s5f$	0.006
	$3d4f^2$	0.004		$3d4d4f$	0.005
	$3d4f^2$	-0.004		$3d4p5g$	-0.004
$3d^2 4s$	$3d^2 4d$	0.018			
	$3d4s4d$	0.016			
	$3d4s5g$	0.01			
	$3d^2 4d$	0.009			
	$3d4d5g$	-0.004			
	$3d^2 5d$	-0.004			
	$3d4d5g$	0.004			
	$3d4d5g$	0.004			

Conclusions

- The wave functions of the ground and 33 excited staes of the singly ionized vanadium were calculated in scope of non-relativistic LS appoximation using the MCHF method and CI approach
- The calculated values of the excitation energies are in good agreement with the available experimental data
- For the multi-configuration expansions for each of four types of electronic configurations under considerations ($3d^3$, $3d^2 4s$, and $3d^2 4p$) the main correlation contributions were investigated
- Obtained sets of the wave functions can be used in further calculations of
  - radiative parameters of V_{III} -lines
  - low-energy electron scattering by vanadium ion (non-relativistic or quasi-relativistic approach with recoupling procedure)
  - wave functions of V_{II} using BSR method