Accurate estimations of circumstellar and interstellar lines of quadruply ionized vanadium using the coupled cluster approach

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ABSTRACT

Accurate *ab initio* calculations have been carried out to study the valence electron removal energies and oscillator strengths of astrophysically important electromagnetic transitions of quadruply ionized vanadium, V^{4+}. Many important electron correlations are considered to all-orders using the relativistic coupled-cluster theory. Calculated ionization potentials and fine structure splittings are compared with the experimental values, wherever available. To our knowledge, oscillator strengths of electric dipole transitions are predicted for the first time for most of the transitions. The transitions span in the range of ultraviolet, visible and near infrared regions and are important for astrophysical observations.

Subject headings: atomic data — stars: circumstellar matter — ISM: atoms

1. Introduction

Vanadium (V) is very important constituent in the atmosphere of dwarf stars (Kirkpatrick et al. 1999) as it condenses into solid solution with Ti-bearing condensates (as observed in meteorites) and not as pure vanadium oxide (V_2O_5) as commonly assumed. Abundance of V in its ionic or molecular form is used to constrain temperature (Lodders 2002) at the dwarf transition. The abundance of V has been seen for 46 normal stars of spectral types from G8 to M0, and their accurate estimates depend on the precise evaluation of transition amplitudes. This abundance is very important in Sun (Bonsack 1959) and the observed maximum abundance among similar stars declines with surface temperature. The abundance excesses of this odd Z element by 1.2 dex in the hot peculiar star, like 'star 3 cen A', has very interesting and important applications in astrophysics (Cowley & Wahlgern 2002). The transition between low-lying energy levels is also of importance to the identification of V emission lines in solar

spectra. Spectroscopic studies of this multi-charged ion are important in numerous applications in laser and plasma physics apart from astrophysics, like, the operations of short-wave laser plasma, plasma diagnostics etc (Vainshtein et al. 1986).

The dominant configuration to the ground state of quadruply ionized vanadium (V^{4+}) is [Ar]$3d_{3/2}$ ($^2D_{3/2}$), with strong correlations from $3d$ orbitals. This is unlike the isoelectronic neutral potassium (K), whose ground state is dominated by [Ar]$4s_{1/2}$ ($^2S_{1/2}$). Experimental ionization potentials (IP) of ground and excited states of this ion (Deurzen 1977) are tabulated in the NIST web database (NIST website reference). The comparison highlights the effective considerations of quantum many-body theories, especially the correlation contributions applied to evaluate these energy eigenstates. There is no line strength estimation among different low lying states obtained from the change of outer most valence orbitals of V^{4+} to our knowledge. For few transitions, preliminary semi-empirical results are available wherein experimental energies had been used to calculate oscillator strengths (Malinovskaya et al. 1992).

Here we have employed the relativistic coupled cluster method with single and double excitations (RCCSD). This is one of the most powerful highly correlated approaches due to its all order behavior for the correlation operator (Lindgren and Morrison 1985). The all order behavior comes from the generation of correlated RCCSD states using exponential structure of the cluster operators over the Dirac-Fock (DF) reference states (Coester 1958), which is explicitly explained in our recent paper (Sahoo et al. 2004). The contributions due to Breit interaction (Breit 1929) which is four orders smaller than the Coulomb interaction have been neglected. For a univalent atomic system a set of coupled equations for the cluster operators, T_n, may be obtained from the Bloch equations for core and valence electrons separately (Lindgren and Morrison 1985; Debasish et al. 1989). Because of this consideration, though the cluster operators are only of single and double excitations kind, their combinations can produce partial triple excitations which nominate the method as coupled cluster method with single, double and partial triple excitations (CCSD(T)). Contributions from these partial excitations in the ionization potentials (IPs) for other systems are well known (Bartlett 1989); this technique has been described extensively in one of our recent papers (Sahoo et al. 2004). Therefore, it can take into account of different electron correlations, like core correlation, core polarization and pair correlation, effects exhaustively for specific type of excitations (Sahoo et al. 2004).

The oscillator strength for a transition from $|\Psi_i\rangle$ to $|\Psi_f\rangle$ is

$$f_{fi} = \frac{2}{3g_i}\Delta E_{fi} \times |D_{fi}|^2 \tag{1}$$

where ΔE_{fi} is the energy difference between final and initial states and $g_i = 2J_i + 1$ is the

degeneracy factor of the initial state with angular momentum J_i. The electric dipole moment matrix element D_{fi} is defined as

$$D_{fi} \;=\; \frac{\langle\Psi_f|\mathbf{d}|\Psi_i\rangle}{\sqrt{\langle\Psi_f|\Psi_f\rangle}\sqrt{\langle\Psi_i|\Psi_i\rangle}} \tag{2}$$

where,

$$\langle\Psi_f|\mathbf{d}|\Psi_i\rangle \;=\; \langle\Phi_f|e^{T_f^\dagger}de^{T_i}|\Phi_i\rangle \tag{3}$$

$\mathbf{d}$= $e\vec{\mathbf{r}}$ is the electric dipole moment operator in the length (L) gauge form. $|\Phi\rangle$s' are the DF reference states. Similarly, transition matrix elements can be obtained by replacing $\mathbf{d}$ in velocity gauge form (Lin 1978; W. R. Johnson et al. 2002). The connected parts of this expression will contribute and hence we only compute those parts in our dipole matrix element calculations.

In the astrophysical literature, one uses weighted oscillator strength which is the product of degeneracy of the initial state and the oscillator strength and is symmetric with respect to initial and final states. i.e.,

$$gf = (2J_i + 1)f_{if} = -(2J_f + 1)f_{fi}. \tag{4}$$

2. Results and Discussion

We have started with the generation of DF orbitals constructed as linear combination of Gaussian type orbitals (GTOs), given by Chaudhuri et al. (R.K. Chaudhuri et al. 2000). The number of single particle orbital bases are chosen for different symmetries based on the number of occupied orbitals and requirement of the transitions of interest. All the core orbitals are considered active in our calculations to make correlations more exhaustive, especially the core correlation part. Table I shows the excitation energies and fine structure splittings of many low lying states with single unfilled orbitals of V^{4+}. For ionization potentials, we find very good agreement with the experimental data obtained from NIST database (NIST website reference) for all the cases. Leaving out the $3d_{5/2}$ state which has rather low binding energy, the average deviation from the experimental values are about 0.1%. The experimental uncertainty of the allowed transition wavelengths in the NIST values are very small, at the level of 2nd to 3rd decimal places, which are of the order 10 cm^{-1} in excitation energies. The fine-structure splittings are of the same order. Therefore, it is important to do higher precession experiments for fine-structure splittings.

The oscillator strength for transitions between different energy states depend linearly on energy, and quadratically on the electric dipole matrix elements (Eq. (1)). This shows

Table 1: Ionization Potentials(IPs) and fine structure (FS) splittings (in cm^{-1}) of V^{+4} and their comparison with NIST values. The percentage of differences of our calculated IP results compared to NIST results are shown in parenthesis on the side of CCSD(T) IP results.

	IP		FS	
States	CCSD(T)	NIST	CCSD(T)	NIST
$3d_{3/2}$	000.00(0.00)	000.00		
$3d_{5/2}$	707.63(13.24)	624.87	707.63	624.87
$4s_{1/2}$	147728.21(0.28)	148143.35		
$4p_{1/2}$	206489.02(0.04)	206393.72		
$4p_{3/2}$	207779.93(0.05)	207660.00	1290.91	1266.28
$4d_{3/2}$	293925.55(0.00)	293902.86		
$4d_{5/2}$	294082.10(0.01)	294047.24	156.54	144.38
$5s_{1/2}$	328103.19(0.03)	328217.30		
$5p_{1/2}$	351832.99(0.09)	351500.51		
$5p_{3/2}$	352318.34(0.08)	352018.34	485.34	517.83
$5d_{3/2}$	388227.86(0.06)	387977.07		
$5d_{5/2}$	388300.23(0.06)	388043.69	72.37	66.62
$6s_{1/2}$	404449.78(0.14)	403855.12		
$6p_{1/2}$	415612.86(0.04)	415420.10		
$6p_{3/2}$	415591.43(0.02)	415675.69	21.43	225.59
$4f_{5/2}$	347524.11(0.61)	349675.57		
$4f_{7/2}$	347500.44(0.50)	349252.40	23.67	423.17
$5g_{7/2}$	414969.56(0.33)	416360.29		
$5g_{9/2}$	414963.83(0.33)	416361.78	05.73	01.49
$6d_{3/2}$	434623.00(0.07)	434303.77		
$6d_{5/2}$	434653.58(0.07)	434340.92	30.58	37.15
$6g_{7/2}$	450047.94(0.00)	450024.54		
$6g_{9/2}$	450043.64(0.00)	450025.20	04.30	00.64

the necessity to calculate transition matrix elements appropriately. We present the electric dipole transition amplitudes in both length and velocity gauges in Table II. The good agreement between these two forms from the calculations using the same initial and final wavefunctions highlights the fact that the numerical algorithm is robust. A detailed derivation and interpretation of different gauges can be found in (Bethe and Salpeter 1957), and in few recent references (W. R. Johnson et al. 2002). The little differences in the values of these two forms for particular transition amplitude may be improved by considering negative energy states in the calculation. In few transition amplitudes, there are considerable disagreement between the length- and velocity-forms. The detail analysis might be possible using the approach suggested by (Savukov and Johnson 2000). In table III, we have given the *ab initio* oscillator strengths (f-value) for 'ground to excited' and 'excited to excited' transitions, which are also astrophysically important. Here we are presenting the oscillator strength in the length gauge due to its comparative fast convergence (Das & Idress 1990).

3. Conclusion

Highly correlated relativistic coupled cluster theory has been employed to study the oscillator strengths of the astrophysically important electric dipole transitions. To our knowledge these are the first calculations of oscillator strengths for most of the transitions presented here. All the transitions are in the ultraviolet, visible or near infrared regions. The good agreement between transition amplitudes obtained from length and velocity gauge expressions highlight the accuracies of our computational method. This work will motivate astronomers to observe these lines of V^{4+} to predict the abundances of these species in astronomical bodies and experimentalists to verify our results.

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Table 2: Comparisons between length and velocity gauge transition amplitudes.

Terms		Length	Velocity	Terms		Length	Velocity
$4s_{1/2}$	$\rightarrow 4p_{1/2}$	1.74965	1.75033	$4d_{3/2}$	$\rightarrow 4p_{1/2}$	2.76747	2.84837
	$\rightarrow 5p_{1/2}$	0.23476	0.21403		$\rightarrow 5p_{1/2}$	2.18131	1.99049
	$\rightarrow 6p_{1/2}$	0.05003	0.03953		$\rightarrow 6p_{1/2}$	0.10890	0.07280
	$\rightarrow 4p_{3/2}$	-2.47677	-2.36660		$\rightarrow 4p_{3/2}$	1.24409	1.19310
	$\rightarrow 5p_{3/2}$	-0.31660	-0.38246		$\rightarrow 5p_{3/2}$	0.96719	0.96266
	$\rightarrow 6p_{3/2}$	-0.07101	-0.07757		$\rightarrow 6p_{3/2}$	0.05241	0.05954
$3d_{3/2}$	$\rightarrow 4p_{1/2}$	-0.70241	-0.48866		$\rightarrow 4f_{5/2}$	-4.44233	-4.51143
	$\rightarrow 5p_{1/2}$	-0.19265	-0.07370	$4d_{5/2}$	$\rightarrow 4p_{3/2}$	3.73203	3.53595
	$\rightarrow 6p_{1/2}$	-0.09081	-0.04798		$\rightarrow 5p_{3/2}$	2.90946	2.93882
	$\rightarrow 4p_{3/2}$	-0.31147	-0.28369		$\rightarrow 6p_{3/2}$	0.14753	0.17376
	$\rightarrow 5p_{3/2}$	0.08668	0.08420		$\rightarrow 4f_{5/2}$	1.18770	1.20082
	$\rightarrow 6p_{3/2}$	0.02889	0.10971		$\rightarrow 4f_{7/2}$	5.30192	5.38146
	$\rightarrow 4f_{5/2}$	0.67548	0.79536	$4f_{5/2}$	$\rightarrow 5g_{7/2}$	-5.63172	-5.19379
$3d_{5/2}$	$\rightarrow 4p_{3/2}$	-0.93952	-0.95399		$\rightarrow 6g_{7/2}$	-1.84114	-1.55890
	$\rightarrow 5p_{3/2}$	0.26166	0.34994	$4f_{7/2}$	$\rightarrow 5g_{7/2}$	-1.08111	-0.99647
	$\rightarrow 6p_{3/2}$	0.14228	0.10591		$\rightarrow 6g_{7/2}$	-0.35363	-0.29909
	$\rightarrow 4f_{5/2}$	-0.17964	-0.19236		$\rightarrow 5g_{9/2}$	6.39624	5.89684
	$\rightarrow 4f_{7/2}$	-0.81273	-0.97714		$\rightarrow 6g_{9/2}$	2.09246	1.77063
$5s_{1/2}$	$\rightarrow 4p_{1/2}$	0.91525	0.86305	$5d_{3/2}$	$\rightarrow 4p_{1/2}$	-0.05739	-0.15377
	$\rightarrow 5p_{1/2}$	3.45262	3.41492		$\rightarrow 5p_{1/2}$	5.14639	5.08534
	$\rightarrow 6p_{1/2}$	-0.09268	-0.08414		$\rightarrow 6p_{1/2}$	-1.07982	-0.96877
	$\rightarrow 4p_{3/2}$	-1.31827	-1.35452		$\rightarrow 4p_{3/2}$	-0.01914	-0.02498
	$\rightarrow 5p_{3/2}$	-4.87908	-4.72249		$\rightarrow 5p_{3/2}$	2.31138	2.20311
	$\rightarrow 6p_{3/2}$	0.13169	0.14329		$\rightarrow 6p_{3/2}$	-0.48293	-0.46061
$6s_{1/2}$	$\rightarrow 4p_{1/2}$	0.27420	0.24626		$\rightarrow 4f_{5/2}$	-2.44997	-2.39345
	$\rightarrow 5p_{1/2}$	-1.58072	-1.67907	$5d_{5/2}$	$\rightarrow 4p_{3/2}$	-0.06172	0.09229
	$\rightarrow 6p_{1/2}$	1.58456	1.31189		$\rightarrow 5p_{3/2}$	6.93100	6.58011
	$\rightarrow 4p_{3/2}$	-0.39158	-0.43908		$\rightarrow 6p_{3/2}$	-1.44693	-1.38397
	$\rightarrow 5p_{3/2}$	2.41224	2.34950		$\rightarrow 4f_{5/2}$	0.65354	0.64360
	$\rightarrow 6p_{3/2}$	-2.22873	-1.82955		$\rightarrow 4f_{7/2}$	2.91305	2.85422
$6d_{3/2}$	$\rightarrow 4p_{1/2}$	-0.03437	-0.04741	$6d_{5/2}$	$\rightarrow 4p_{3/2}$	0.05564	0.16646
	$\rightarrow 5p_{1/2}$	0.36454	0.37956		$\rightarrow 5p_{3/2}$	0.46061	0.26962
	$\rightarrow 6p_{1/2}$	2.32712	1.96753		$\rightarrow 6p_{3/2}$	3.10432	2.56486
	$\rightarrow 4p_{3/2}$	0.01925	0.05307		$\rightarrow 4f_{5/2}$	0.11103	0.11702
	$\rightarrow 5p_{3/2}$	0.15162	0.09272		$\rightarrow 4f_{7/2}$	0.49502	0.51231
	$\rightarrow 6p_{3/2}$	1.03434	0.85524				
	$\rightarrow 4f_{5/2}$	-0.41493	-0.42212				

Table 3: Transition wavelengths and oscillator strengths of V^{4+}.

Terms		λ_{NIST}(Å)	λ_{CCSD}(Å)	gf-value
$4s_{1/2}$	$\rightarrow 4p_{1/2}$	1716.72	1701.81	0.5464
	$\rightarrow 4p_{3/2}$	1680.20	1665.23	1.1189
	$\rightarrow 5p_{1/2}$	491.74	489.94	2.9499
	$\rightarrow 5p_{3/2}$	490.49	448.78	6.2293
	$\rightarrow 6p_{1/2}$	374.14	373.29	2.0368
	$\rightarrow 6p_{3/2}$	373.78	373.32	0.0041
$3d_{3/2}$	$\rightarrow 4p_{1/2}$	484.51	484.28	0.3094
	$\rightarrow 4p_{3/2}$	481.55	481.27	0.0612
	$\rightarrow 5p_{1/2}$	284.49	284.22	0.8901
	$\rightarrow 5p_{3/2}$	284.07	283.83	0.0080
	$\rightarrow 6p_{1/2}$	240.72	240.60	0.0104
	$\rightarrow 6p_{3/2}$	240.57	240.62	0.0010
	$\rightarrow 4f_{5/2}$	285.97	287.74	0.4816
$3d_{5/2}$	$\rightarrow 4p_{3/2}$	483.00	482.92	0.5552
	$\rightarrow 5p_{3/2}$	284.58	284.40	0.0731
	$\rightarrow 6p_{3/2}$	240.93	241.03	0.0255
	$\rightarrow 4f_{5/2}$	286.49	288.33	0.0339
	$\rightarrow 4f_{7/2}$	286.83	288.35	0.6958
$5s_{1/2}$	$\rightarrow 4p_{1/2}$	820.85	822.27	0.3094
	$\rightarrow 4p_{3/2}$	829.48	831.09	0.6351
	$\rightarrow 5p_{1/2}$	4294.94	4214.11	0.8592
	$\rightarrow 5p_{3/2}$	4201.49	4129.64	1.7510
	$\rightarrow 6p_{1/2}$	1146.75	1142.73	0.0022
	$\rightarrow 6p_{3/2}$	1143.40	1143.01	0.0040
$6s_{1/2}$	$\rightarrow 4p_{1/2}$	506.42	505.15	0.0452
	$\rightarrow 4p_{3/2}$	509.69	508.46	0.0916
	$\rightarrow 5p_{1/2}$	1910.05	1900.53	0.3993
	$\rightarrow 5p_{3/2}$	1929.13	1918.22	0.9214
	$\rightarrow 6p_{1/2}$	8646.79	8958.09	0.0851
	$\rightarrow 6p_{3/2}$	8459.82	8975.33	0.1681
$4f_{5/2}$	$\rightarrow 5g_{7/2}$	1499.59	1541.18	6.2510
	$\rightarrow 6g_{7/2}$	996.52	959.71	1.0728

Terms		λ_{NIST}(Å)	λ_{CCSD}(Å)	gf-value
$4d_{3/2}$	$\rightarrow 4p_{1/2}$	1142.73	1143.68	2.0341
	$\rightarrow 4p_{3/2}$	1159.51	1160.82	0.4050
	$\rightarrow 5p_{1/2}$	1736.18	1726.89	0.8369
	$\rightarrow 5p_{3/2}$	1720.71	1712.54	0.1659
	$\rightarrow 6p_{1/2}$	822.92	821.77	0.0043
	$\rightarrow 6p_{3/2}$	821.53	821.92	0.0010
	$\rightarrow 4f_{5/2}$	1792.99	1865.72	3.2129
$4d_{5/2}$	$\rightarrow 4p_{3/2}$	1157.57	1158.71	3.6512
	$\rightarrow 5p_{3/2}$	1724.99	1717.14	1.4974
	$\rightarrow 6p_{3/2}$	822.17	822.98	0.0080
	$\rightarrow 4f_{5/2}$	1797.64	1871.18	0.2289
	$\rightarrow 4f_{7/2}$	1811.42	1872.01	4.5612
$4f_{7/2}$	$\rightarrow 5g_{7/2}$	1490.13	1540.61	0.2304
	$\rightarrow 5g_{9/2}$	1490.10	1446.24	8.5927
	$\rightarrow 6g_{7/2}$	992.33	959.49	0.0395
	$\rightarrow 6g_{9/2}$	992.33	975.19	1.3638
$5d_{3/2}$	$\rightarrow 4p_{1/2}$	550.71	550.24	0.0018
	$\rightarrow 4p_{3/2}$	554.57	554.17	0.0002
	$\rightarrow 5p_{1/2}$	2741.48	2747.64	2.9279
	$\rightarrow 5p_{3/2}$	2780.96	2784.77	0.5827
	$\rightarrow 6p_{1/2}$	3643.91	3651.63	0.0969
	$\rightarrow 6p_{3/2}$	3610.28	3654.49	0.0193
	$\rightarrow 4f_{5/2}$	2610.86	2656.77	0.7421
$5d_{5/2}$	$\rightarrow 4p_{3/2}$	554.37	553.95	0.0020
	$\rightarrow 5p_{3/2}$	2775.82	2779.17	5.2505
	$\rightarrow 6p_{3/2}$	3618.99	3664.18	0.1735
	$\rightarrow 4f_{5/2}$	2606.33	2452.41	0.0529
	$\rightarrow 4f_{7/2}$	2577.89	2450.98	1.0516
$6d_{3/2}$	$\rightarrow 4p_{1/2}$	438.76	438.33	0.0008
	$\rightarrow 4p_{3/2}$	441.22	440.83	0.0002
	$\rightarrow 5p_{1/2}$	1207.68	1207.87	0.0334
	$\rightarrow 5p_{3/2}$	1215.28	1214.99	0.0057
	$\rightarrow 6p_{1/2}$	5295.58	5260.35	0.3127
	$\rightarrow 6p_{3/2}$	5368.23	5254.42	0.0618
	$\rightarrow 4f_{5/2}$	1181.63	1148.12	0.0455
$6d_{5/2}$	$\rightarrow 4p_{3/2}$	441.14	440.83	0.0021
	$\rightarrow 5p_{3/2}$	1214.73	1214.98	0.0530
	$\rightarrow 6p_{3/2}$	5360.42	5254.26	0.5571
	$\rightarrow 4f_{5/2}$	1181.26	1148.11	0.0032
	$\rightarrow 4f_{7/2}$	1175.38	1147.80	0.0648