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THE SPECTRUM AND ENERGY LEVELS OF QUADRUPLE IONIZED VANADIUM (V V)*

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ABSTRACT

The spectrum of V V has been observed by using a vacuum sliding spark at 1000-A peak current. Sixty-one lines in the region 480-8500 Å have been observed to make transitions between 29 levels, nineteen of which are new. The ionization energy is revised to 526 524±5 cm^{-1}. An isoelectronic comparison confirms the inversion of the $3p^6 4f\ ^2F^o_{5/2,7/2}$ levels as being caused by their interaction with those of the $^2F^o$ term in the $3p^5 3d^2$ configuration.

INDEX HEADINGS: vanadium, energy levels, spectra, wavelengths, ultraviolet.

INTRODUCTION

The V^{4+} ion has a ground state [Ar] $3d^1\ ^2D_{3/2}$ and is isoelectronic with neutral potassium. The known data have consisted of 15 classified lines in the region between 286 and 1811 Å, eleven of which were observed by Gibbs and White[1] and four by Iglesias,[2] from which eight levels were deduced. The development of a precisely controllable vacuum sliding spark[3] has made the renewed investigation of the spectrum practical.

EXPERIMENTAL DETAILS

To excite and separate the spectra of vanadium a vacuum sliding spark light source was used connected in a series LCR electrical circuit. The source, its mode of operation, behavior, and ability to excite and separate higher ionized atomic states as the circuit parameters L, C, R, and the voltage V_o across the capacitor are varied have been described.[4] Lines belonging to a given state of ionization were identified by observing their common intensity behavior with current. Spectrum lines of oxygen, silicon, and carbon were also present as a result of the excitation of the spacer material, especially at peak currents greater than 400 A. To obtain good excitation of V V, a peak current of 1000 A was selected. The electrical circuit parameters were $L = 13\ \mu h$, $C = 24\ \mu f$, external resistance $R < 1\ \Omega$, and $V_o = 1350$ V. The duration of the current pulse (full width at half maximum) was 56 μsec and the repetition rate was 15 sec^{-1}. The spectrum was photographed from 450 to 2800 Å with a 3-m normal-incidence vacuum spectrograph (3 Å/mm plate factor), and from 2600 to 8500 Å with a 3.4-m Ebert mounted plane grating in air (5 Å/mm). Exposures were 400 pulses.

Wavelength standards shorter than 2700 Å were obtained from a water-cooled copper hollow cathode; for wavelengths longer than 2700 Å a thorium iodide lamp was used. Twenty-five to 40 calibration lines were used on each 25-cm plate. Their wavelengths were fitted to a sixth-order polynomial. The error limits assigned to the vanadium wavelengths were estimated on the basis of external consistency to be 0.004 Å in the vacuum region, and 0.008 Å in air. We have made no systematic study of line widths or wavelength shifts as functions of source parameters, but we exercised great care in making source conditions identical when taking spectrograms for wavelength measurements.

Spectrum line intensities are visual estimates on a scale from 1 to 100.

OBSERVATIONS AND ANALYSIS

The analysis was started on the basis of the levels previously reported by Gibbs and White, and a study of isoelectronic and quantum-defect regularities. The lowest unknown levels were predicted from known isoelectronic data with a possible error of the order of 100 cm^{-1} in addition to the uncertainty in ionization energy. Fine structure intervals were predicted from the near constancy of the difference for the two components of a doublet term in a Rydberg series. The observed lines were then classified to establish the first three members of a series. At this point the higher levels of a series could be predicted and the ionization energy calculated. Remaining observed lines were then classified to establish these higher levels. In Table I are listed 59 classified lines of V VI, 46 of which are newly classified. Several unclassified lines whose intensity behavior is similar to that of V VI lines are listed in Table II. The lines marked h appeared hazy, apparently caused by blending with impurity lines or with lines from lower ionization stages. The line at 4293.74 Å is blended with a V III line at 4293.47 Å. The wavelengths reported by Gibbs and White for the 483 Å triplet and 590 Å doublet are about

0.1 Å too large and 0.3 Å too small, respectively, and the lines at 285 Å and 286 Å (3d-4f) were wrongly classified; the 4f levels are inverted in V VI. Four transitions between the $3p^6$ and $3p^5 3d^2$ configurations were observed. The triplet at 962 Å has been classified as the $3p^6 4d\ ^2D - 3p^5 3d^2\ ^2F^o$ combination and places the latter term about 80 cm^{-1} below the value reported by Gabriel, Fawcett, and Jordan.[5] The line at 5442 Å has been tentatively assigned to the $3p^6 5g\ ^2G_{9/2} - 3p^5 3d^2\ ^2F^o_{7/2}$ transition, which would constitute a double electron jump. No transitions were observed between the levels reported here and the $3p^5 3d^2\ ^2D^o$ term reported in Ref. 5. The 19 newly found levels and the corrected values for the previously reported levels are presented in Table III. The uncertainty in the levels relative to the ground state is estimated to be 3 cm^{-1}, resulting chiefly from the uncertainty in the 4p-3d triplet; the internal consistency of other closed combination cycles is a few units in the first decimal place of the wavenumber. Some of the levels have been established by a single transition. An energy level diagram is presented in Fig. 1.

IONIZATION ENERGIES AND SERIES FORMULAS

The ionization energy can be calculated from a series that is assumed to be described by a Ritz-like formula, and extrapolating the series to the limit $n = \infty$. We used the extended Ritz formula

$$\delta_n \equiv n - n^* = \sum_{i=0} a_i\ t_n^{\ i}$$

$$t_n \equiv \frac{T_n}{R} = \left(\frac{Z_c}{n^*}\right)^2$$

where T_n is the wavenumber of the nth term in the series, R is the mass-corrected Rydberg constant, and Z_c is the net core charge. We used $R = (109\ 737.31 - 60.22/50.942)\ cm^{-1}$ and $Z_c = 4$. The ionization energy of each level series was calculated using all of the observed levels in each series.[6] The ng series, which reaches closest to the limit and is representable by the least number of quantum-defect constants, is assumed to give the best value of the ionization energy. The results are given in Table IV. The ionization energy derived from the np $^2P^o_{3/2}$ series is 22 cm^{-1} less than the value derived from the np $^2P^o_{1/2}$ series, and both are about 500 cm^{-1} less than the values obtained from the ng and ns series. We think this is due to a depression of these ^2P series caused by a perturbing level(s) located above the 6p $^2P^o$ term; the perturbation is most likely caused by the $3p^5 3d^2(^2P^o, {}^4P^o)$ terms. The ionization energies derived from the 3d-6d terms are about 300 cm^{-1} too large. The possible error in the ionization energy derived from the ng series is estimated to be a few cm^{-1} owing to the uncertainty in the wavenumbers derived from the 4p-3d and 4f-ng transitions. The value we adopt is $E_{ion} = 526\ 524 \pm 5\ cm^{-1}$.

ISOELECTRONIC SEQUENCE

With the spectra of K I, Ca II, Sc III, and Ti IV well analyzed,[3,7,8,9] it is possible to observe how the V VI energy levels fit into the neutral potassium isoelectronic sequence. Figure 2 shows the trends for selected levels of $3p^6 n\ell$. Levels belonging to two other configurations, $3p^5 3d^2$ and $3p^5 3d4s$ have also been plotted.[5,10,11] Evidently the depression and inversion of the $3p^6 4f\ ^2F^o$ levels in V VI are due to the perturbing interaction of the

$3p^5 3d^2\ {}^2F^o$ levels. This mutual repulsion was first recognized in Cr VI by Gabriel, Fawcett, and Jordan.[5] The more sensitive plots of $T^H - T + aZ_c$ and $(\Delta E)^{1/4}$ vs. Z_c of Fig. 3 further illustrate the point (T^H is the hydrogenic term value). Other members of the $3p^6nf$ series are expected to be perturbed also.

FOOTNOTES AND REFERENCES

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Table I. Classified lines of V IV. In the intensity column, the symbols mean: h-hazy, b-blend, w-wide.

Level Combination odd - even	Wave number (cm^{-1})	Wavelength (Å)	Intensity
$4f\,^2F_{5/2}$ - $3d\,^2D_{3/2}$	349675	285.98	1
$4f\,^2F_{7/2}$ - $3d\,^2D_{5/2}$	348628	286.84	2
$4p\,^2P_{3/2}$ - $3d\,^2D_{3/2}$	207660.2	481.556	3
$4p\,^2P_{3/2}$ - $3d\,^2D_{5/2}$	207035.9	483.008	30
$4p\,^2P_{1/2}$ - $3d\,^2D_{3/2}$	206393.7	484.511	20
$5p\,^2P_{3/2}$ - $4s\,^2S_{1/2}$	203874.6	490.498	4
$5p\,^2P_{1/2}$ - $4s\,^2S_{1/2}$	203356.6	491.747	2
$4p\,^2P_{1/2}$ - $6s\,^2S_{1/2}$	197461.0	506.429	1
$4p\,^2P_{3/2}$ - $6s\,^2S_{1/2}$	196196	509.694	2
$4p\,^2P_{1/2}$ - $5s\,^2S_{1/2}$	121822.9	820.864	20
$6p\,^2P_{3/2}$ - $4d\,^2D_{3/2}$	121773.0	821.200	1
$6p\,^2P_{3/2}$ - $4d\,^2D_{5/2}$	121628	822.18	6h
$6p\,^2P_{1/2}$ - $4d\,^2D_{3/2}$	121516.7	822.932	3
$4f\,^2F_{7/2}$ - $7g\,^2G$	121080.7	825.895	2
$4f\,^2F_{5/2}$ - $7g\,^2G_{7/2}$	120656.7	828.798	1
$4p\,^2P_{3/2}$ - $5s\,^2S_{1/2}$	120556.6	829.486	30
$3p^5 3d^2\ ^2F_{7/2}$ - $4d\,^2D_{5/2}$	103946.2	962.036	15
$3p^5 3d^2\ ^2F_{5/2}$ - $4d\,^2D_{3/2}$	102232.0	978.168	10
$3p^5 3d^2\ ^2F_{5/2}$ - $4d\,^2D_{5/2}$	102087.6	979.551	1
$4f\,^2F_{7/2}$ - $6g\,^2G$	100771.5	992.344	10
$4f\,^2F_{5/2}$ - $6g\,^2G_{7/2}$	100348.0	996.532	5
$5p\,^2P_{1/2}$ - $7s\,^2S_{1/2}$	91575	1092.00	1h

(Continued)

Table I (continued)

Level Combination odd - even	Wave number (cm^{-1})	Wavelength (Å)	Intensity
$5p\,^2P_{3/2}$ - $7s\,^2S_{1/2}$	91056.3	1098.222	2
$4p\,^2P_{1/2}$ - $4d\,^2D_{3/2}$	87508.7	1142.744	15
$4p\,^2P_{3/2}$ - $4d\,^2D_{5/2}$	86387.0	1157.581	25
$4p\,^2P_{3/2}$ - $4d\,^2D_{3/2}$	86242.5	1159.522	6
$4f\,^2F_{7/2}$ - $5g\,^2G$	67108.8	1490.118	20
$4f\,^2F_{5/2}$ - $5g\,^2G_{7/2}$	66684.2	1499.605	10
$4p\,^2P_{3/2}$ - $4s\,^2S_{1/2}$	59516.6	1680.204	100
$4p\,^2P_{1/2}$ - $4s\,^2S_{1/2}$	58250.4	1716.725	50
$5p\,^2P_{3/2}$ - $4d\,^2D_{3/2}$	58115.5	1720.710	4
$5p\,^2P_{3/2}$ - $4d\,^2D_{5/2}$	57971.2	1724.995	15
$5p\,^2P_{1/2}$ - $4d\,^2D_{3/2}$	57597.6	1736.183	10
$4f\,^2F_{5/2}$ - $4d\,^2D_{3/2}$	55772.9	1792.984	25
$4f\,^2F_{5/2}$ - $4d\,^2D_{5/2}$	55628.5	1797.639	6h
$4f\,^2F_{7/2}$ - $4d\,^2D_{5/2}$	55205.4	1811.418	30
$5p\,^2P_{1/2}$ - $6s\,^2S_{1/2}$	52355.0	1910.038	4
$5p\,^2P_{3/2}$ - $6s\,^2S_{1/2}$	51836.9	1929.126	9
$4f\,^2F_{7/2}$ - $5d\,^2D_{5/2}$	38791.2	2577.130	20
$4f\,^2F_{5/2}$ - $5d\,^2D_{5/2}$	38368.6	2605.523	4h
$4f\,^2F_{5/2}$ - $5d\,^2D_{3/2}$	38301.3	2610.098	10
$5p\,^2P_{1/2}$ - $5d\,^2D_{3/2}$	36476.7	2740.666	10
$5p\,^2P_{3/2}$ - $5d\,^2D_{5/2}$	36025.4	2774.998	15

(Continued)

Table I (continued)

Level Combination odd - even	Wave number (cm^{-1})	Wavelength (Å)	Intensity
$5p\,^2P_{3/2}$ - $5d\,^2D_{3/2}$	35958.8	2780.144	3
$6h\,^2H$ - $5g\,^2G$	33886.8	2950.13	8w
$6p\,^2P_{3/2}$ - $5d\,^2D_{3/2}$	27698.54	3609.269	2
$6p\,^2P_{1/2}$ - $7s\,^2S_{1/2}$	27654.33	3615.039	2h
$6p\,^2P_{3/2}$ - $5d\,^2D_{5/2}$	27631.96	3617.966	15h
$6p\,^2P_{1/2}$ - $5d\,^2D_{3/2}$	27442.94	3642.887	8
$6p\,^2P_{3/2}$ - $7s\,^2S_{1/2}$	27399.03	3648.724	4
$5p\,^2P_{3/2}$ - $5s\,^2S_{1/2}$	23800.99	4200.322	20
$5p\,^2P_{1/2}$ - $5s\,^2S_{1/2}$	23283.2	4293.74	20b
$7h\,^2H$ - $6g\,^2G$	20463.86	4885.299	7w
$6h\,^2H$ - $7i\,^2I$	20276.12	4930.533	15w
$6p\,^2P_{1/2}$ - $6d\,^2D_{3/2}$	18883.64	5294.115	4
$6p\,^2P_{3/2}$ - $6d\,^2D_{5/2}$	18665.21	5356.070	8
$6p\,^2P_{3/2}$ - $6d\,^2D_{3/2}$	18628.07	5366.750	1
$3p^5 3d^2\ ^2F_{7/2}$ - $5g\,^2G_{9/2}$?	18368.12	5442.704	3
$6p\,^2P_{3/2}$ - $6s\,^2S_{1/2}$	11820.50	8457.555	1

Table II. Unclassified lines of V V.

Wavelength (Å)	Wave number (cm^{-1})	Intensity
3316.470	30143.86	10
3363.517	29722.24	6
3966.598	25203.39	5
4106.318	24345.84	3

Table III. Energy levels of V IX. Level values in parentheses indicate predicted but not observed levels.

Symbol	Energy (cm^{-1})	Interval (cm^{-1})	Term Value (cm^{-1})	n^*	Δn^*
$4s\,^2S_{1/2}$	148143.3		378380.7	2.692652	
$5s\,^2S_{1/2}$	328216.9		198307.1	3.719424	
$6s\,^2S_{1/2}$	403854.8		122669.2	4.729084	
$7s\,^2S_{1/2}$	443074.2		83449.8	5.733663	
$8s\,^2S_{1/2}$	(466065)		(60459)		
$4p\,^2P^o_{1/2}$	206393.7	1266.2	320130.3	2.927395	0.005807
$4p\,^2P^o_{3/2}$	207659.9		318864.1	2.933202	
$5p\,^2P^o_{1/2}$	351499.9	518.0	175024.1	3.959095	0.005871
$5p\,^2P^o_{3/2}$	352017.9		174506.1	3.964966	
$6p\,^2P^o_{1/2}$	415419.6	255.6	111104.4	4.969117	0.005725
$6p\,^2P^o_{3/2}$	415675.2		110848.8	4.974842	
$3d\,^2D_{3/2}$	0.0	623.6	526524.0	2.282631	0.001353
$3d\,^2D_{5/2}$	623.6		525900.4	2.283984	
$4d\,^2D_{3/2}$	293902.4	144.4	232621.6	3.434154	0.001066
$4d\,^2D_{5/2}$	294046.8		232477.2	3.435220	
$5d\,^2D_{3/2}$	387976.7	66.6	138547.3	4.449854	0.001070
$5d\,^2D_{5/2}$	388043.3		138480.7	4.450924	
$6d\,^2D_{3/2}$	434303.2	37.2	92220.8	5.454191	0.001100
$6d\,^2D_{5/2}$	434340.4		92183.6	5.455291	
$7d\,^2D_{3/2}$	(460702)	(22.7)	(65822)		
$7d\,^2D_{5/2}$	(460725)		(65799)		

(continued)

Table III (continued)

Symbol	Energy (cm^{-1})	Interval (cm^{-1})	Term Value (cm^{-1})	n^*	Δn^*
$4f\,^2F^\circ_{5/2}$	349675.3	-423.2	176848.7	3.938618	-0.004704
$4f\,^2F^\circ_{7/2}$	349252.1		177271.9	3.933914	
$5g\,^2G_{7/2}$	416359.5	1.4	110164.5	4.990269	0.000032
$5g\,^2G_{9/2}$	416360.9		110163.1	4.990301	
$6g\,^2G$	450023.5		76500.5	5.988426	
$7g\,^2G$	470332.5		56191.5	6.987302	
$8g\,^2G$	(483514)		(43010)		
$6h\,^2H^\circ$	450247.2		76276.8	5.997201	
$7h\,^2H^\circ$	470487.3		56036.7	6.996946	
$7i\,^2I$	470523.3		56000.7	6.999195	
$3p^5 3d^2\ ^2F^\circ_{5/2}$	396134.4	1858.6	130389.6	4.586943	0.033045
$3p^5 3d^2\ ^2F^\circ_{7/2}$	397993.0		128531.0	4.619988	

Table IV. Ionization energies and quantum defect formula constants.

	Δ^a or T_c	Constants[b]	Δ or T_c	Constants	Δ or T_c	Constants	Δ or T_c	Constants
	$^2S_{1/2}$		$^2P_{1/2}$		$^2P_{3/2}$			
4	0.0	1.25766	0.0	1.01920	0.0	1.01400		
5	0.0	1.03935^{-2}	0.0	7.94246^{-3}	0.0	7.25557^{-3}		
6	0.0	1.37402^{-3}	0.0	3.55254^{-3}	0.0	3.75681^{-3}		
7	0.0	-6.07831^{-5}	76883		76740			
8	60459	—	—					
E_{ion}	526517		526039		526017			
	$^2D_{3/2}$		$^2D_{5/2}$		$^2G_{c.g.}$		^2H	
3	0.0	5.41263^{-1}	0.0	5.40023^{-1}				
4	0.0	3.38675^{-3}	0.0	3.62756^{-3}				
5	0.0	1.44223^{-3}	0.0	1.34572^{-3}	0.0	1.58069^{-2}		
6	0.0	1.14660^{-3}	0.0	1.16020^{-3}	0.0	-6.07093^{-3}	0.0	3.75800^{-3}
7	65822		65799		0.0		0.0	-1.37933^{-3}
8	49338		49323		43010		42900	
E_{ion}	526832		526835		526524		526529[c]	

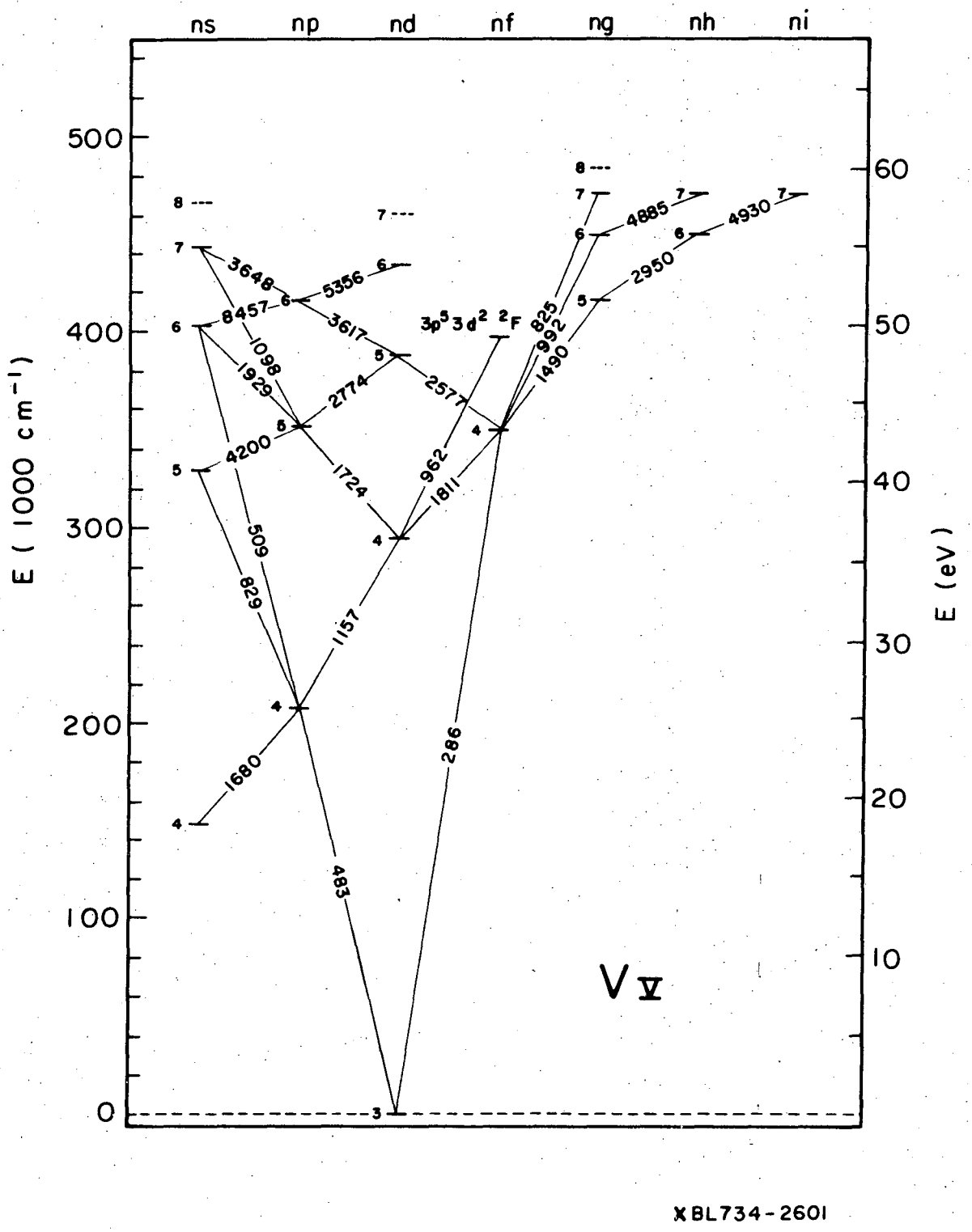
[a] $\Delta \equiv T_c - T_o$. [b] Constants a_i in ascending order for $\delta_n = \sum_{i=0} a_i \left(\frac{T_n}{R}\right)^i$, calculated using the value $E_{ion} = 526524\ cm^{-1}$. [c] Calculated using $\delta_{6h} - \delta_{7h} = -0.00037 \pm 5\%$ as determined from the isoelectronic sequence.[6]

FIGURE CAPTIONS

Fig. 1. Energy level diagram of V V. The figures give the approximate wavelength of the leading line in each multiplet. Dotted lines are predicted levels.

Fig. 2. Selected levels of atoms in the KI isoelectronic sequence.

Fig. 3. Perturbing interactions and fine structure intervals of atoms in the KI isoelectronic sequence.



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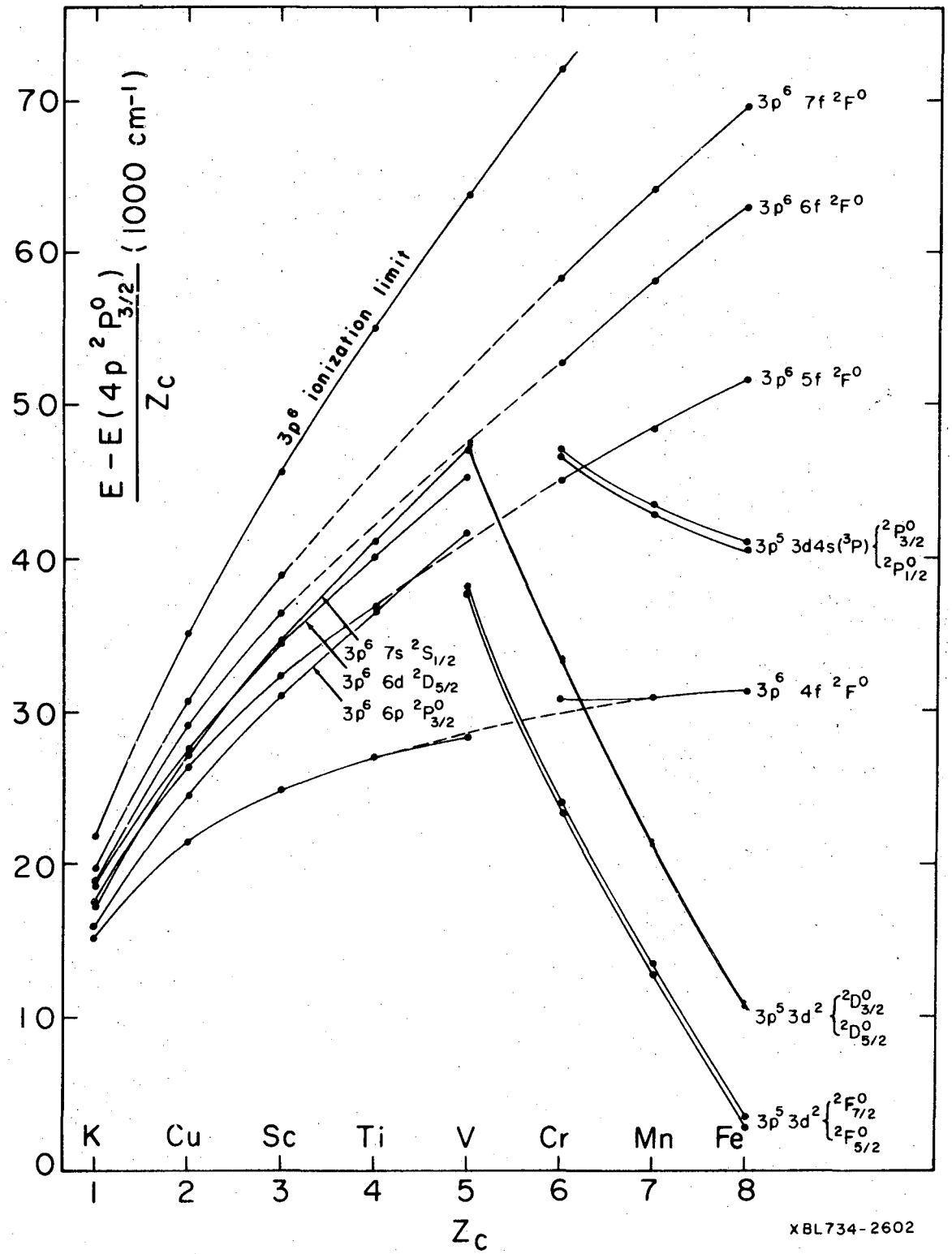

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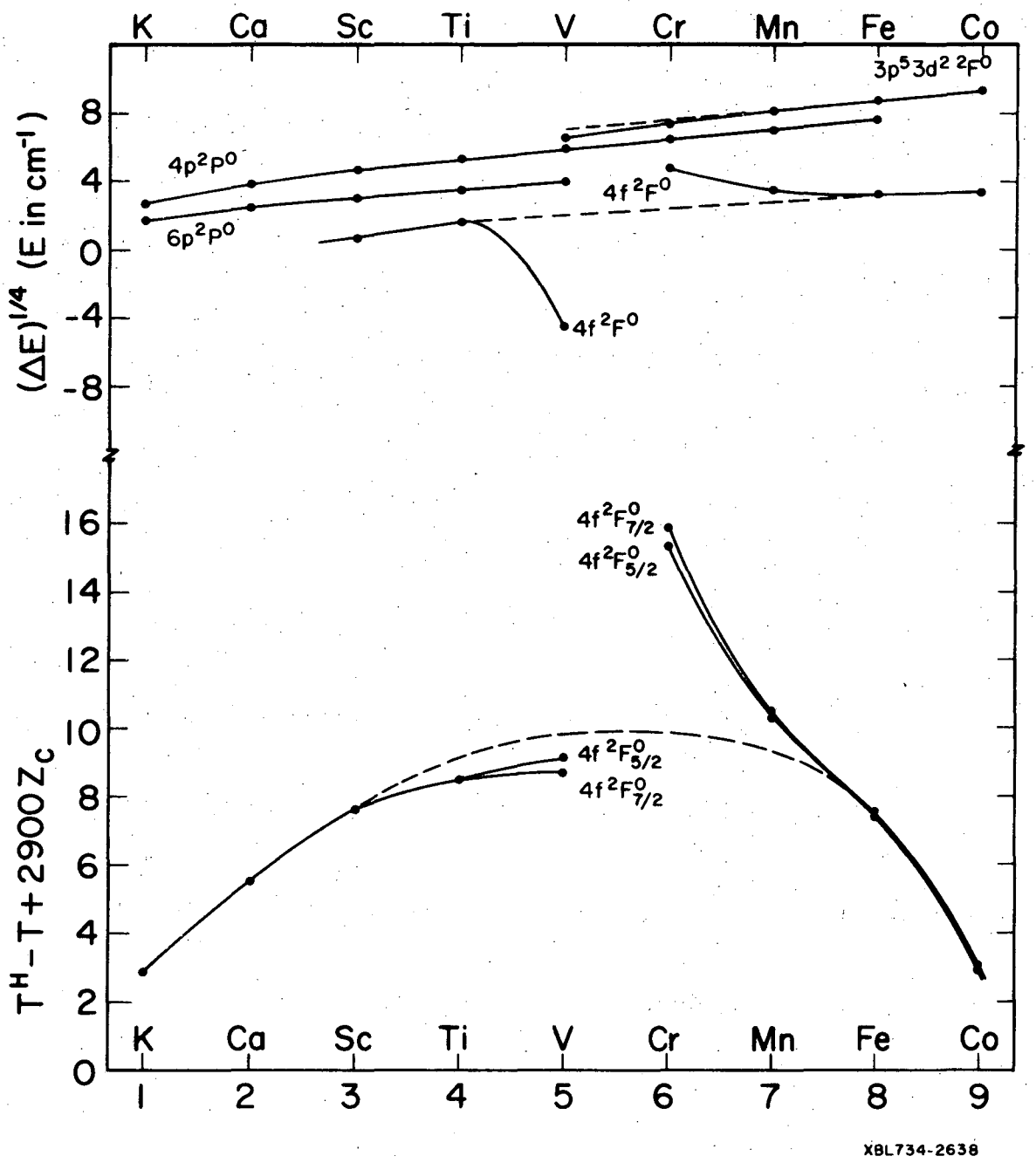

Fig. 3. Perturbing interactions and fine structure intervals of atoms in the KI isoelectronic sequence.

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