PHYSICAL REVIEW A VOLUME 43, NUMBER 5 1 MARCH 1991

Spectrum and energy levels of the xenonlike ion Ce V

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(Received 17 September 1990)

The spectrum of four-times ionized cerium Ce V has been observed with a sliding-spark discharge and a 10.7-m normal-incidence vacuum spectrograph. A total of 107 lines have been classified as transitions between 51 energy levels. All levels of the $5p^6$, $5p^54f$, $5p^55d$, $5p^56s$, $5p^56p$, and $5p^56d$ configurations have been determined. Because of collapse of the $4f$ shell, the $5p^54f$ configuration is situated well below $5p^55d$. *Ab initio* calculations and least-squares fits of the energy parameters to the experimental energy levels are reported. The ionization energy is revised to 527 100±2000 cm^{-1} (65.35±0.25 eV).

INTRODUCTION

The four-times ionized cerium atom Ce V is a member of the xenon isoelectronic sequence. The spectra of the first four ions of this sequence have been analyzed extensively.[1-4] However, in the case of Ce V, only the five resonance lines $5p^6$-$5p^5(5d+6s)$ $J=1$ have been reported.[5] In the present work, we observed the spectrum of Ce V with a sliding-spark discharge and determined the complete level structures of the $5p^6$, $5p^54f$, $5d$, $6s$, $6p$, and $6d$ configurations.

In neutral xenon and the first few members of the Xe isoelectronic sequence the ground state is $5p^6\,{}^1S_0$. Excited configurations are of the type $5p^5nl$. Among these, the $5p^54f$ configuration has a nearly hydrogenic character and lies relatively high in the level system. However, because of the well-known collapse of the $4f$ shell in this region of the Periodic Table,[6] the binding energy of the $5p^54f$ configuration increases dramatically with increasing atomic number Z. The $5p^54f$ configuration plunges downward through the level system and in La IV overlaps $5p^55d$, formerly lowest of the excited configurations. This is illustrated in Fig. 1, where the relative energies of the low $5p^5nl$ configurations of the first five Xe-like ions are plotted. As can be seen, the $5p^54f$ configuration drops rapidly in the level system after Cs II. Because of the proximity of the $5p^54f$ and $5p^55d$ configurations in La IV, many of the $4f$-$5d$ transitions lie in the infrared. This prevented Epstein and Reader[4] from establishing more than six of the twelve levels of $5p^5nf$ in this ion. Our present work extends the knowledge of the $4f$ contraction by means of a comprehensive analysis of the Ce V term system in which all levels of $5p^54f$ have been established.

EXPERIMENT

The spectra were photographed with the 10.7-m normal-incidence vacuum spectrograph at the National Institute of Standards and Technology (NIST). The grating was ruled with 1200 lines/mm. The plate factor was 0.78 Å/mm. The region of observation was 800–3200 Å. The light source was a low-voltage sliding spark between metallic cerium electrodes, operated as described by Reader, Epstein, and Ekberg.[7] Ionization stages of the lines were determined by comparing their intensities at various peak currents in the spark. The spectrum of Ce V was optically excited at a peak current of about 600 Å. Lines of Ce III with wavelengths given by Sugar[8] were used as reference spectra.

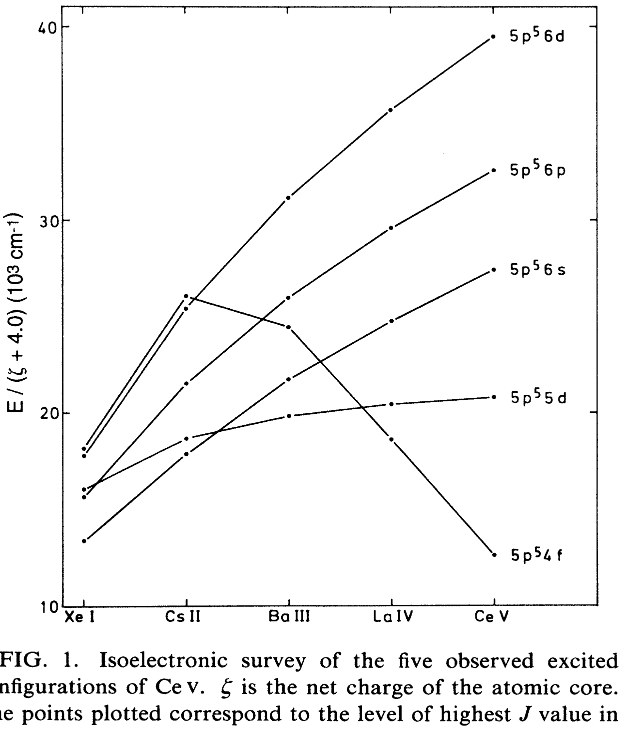

FIG. 1. Isoelectronic survey of the five observed excited configurations of Ce V. ζ is the net charge of the atomic core. The points plotted correspond to the level of highest J value in each configuration. Values are from Refs. 1–4 and the present work. The point for $5p^54f$ of La IV is a value predicted from the known levels of the configuration.

TABLE I. Observed spectral lines of Ce V.

Wavelength (Å)	Intensity[a]	Wave number (cm^{-1})	Classification
365.661[b]	100	273 477.4	$5p^{6}\,{}^{1}S_{0}$–$6s\,1/2\,[1/2]_{1}$
399.361[c]	300	250 399.8	$5p^{6}\,{}^{1}S_{0}$–$5d\,1/2\,[3/2]_{1}$
404.209[c]	150	247 396.8	$5p^{6}\,{}^{1}S_{0}$–$6s\,3/2\,[3/2]_{1}$
482.963[c]	200	207 055.2	$5p^{6}\,{}^{1}S_{0}$–$5d\,3/2\,[3/2]_{1}$
552.134[c]	100	181 115.3	$5p^{6}\,{}^{1}S_{0}$–$5d\,3/2\,[1/2]_{1}$
905.114	10	110 483.3	$5d\,3/2\,[3/2]_{2}$–$6p\,3/2\,[3/2]_{2}$
917.980	100	108 934.8	$5d\,3/2\,[1/2]_{0}$–$6p\,3/2\,[1/2]_{1}$
926.103	30	107 979.3	$5d\,3/2\,[1/2]_{1}$–$6p\,3/2\,[5/2]_{2}$
929.993	10	107 527.6	$5d\,3/2\,[3/2]_{2}$–$6p\,3/2\,[3/2]_{1}$
936.241	80	106 810.1	$4f\,1/2\,[5/2]_{2}$–$5d\,1/2\,[3/2]_{1}$
937.539	6	106 662.2	$5d\,3/2\,[3/2]_{2}$–$6p\,3/2\,[5/2]_{3}$
941.960	170	106 161.6	$5d\,3/2\,[1/2]_{1}$–$6p\,3/2\,[1/2]_{1}$
944.710	270	105 852.6	$5d\,3/2\,[7/2]_{4}$–$6p\,3/2\,[5/2]_{3}$
953.946	40	104 827.8	$5d\,3/2\,[7/2]_{3}$–$6p\,3/2\,[5/2]_{3}$
957.514	60	104 437.1	$5d\,1/2\,[3/2]_{2}$–$6p\,1/2\,[1/2]_{1}$
974.399	10	102 627.4	$5d\,3/2\,[3/2]_{2}$–$6p\,3/2\,[5/2]_{2}$
975.215	100	102 541.5	$5d\,3/2\,[5/2]_{2}$–$6p\,3/2\,[3/2]_{1}$
976.416	10	102 415.4	$5d\,1/2\,[5/2]_{2}$–$6p\,1/2\,[3/2]_{1}$
980.577	150	101 980.8	$5d\,1/2\,[5/2]_{3}$–$6p\,1/2\,[3/2]_{2}$
991.965	100	100 810.0	$5d\,3/2\,[3/2]_{2}$–$6p\,3/2\,[1/2]_{1}$
992.129	200	100 793.4	$5d\,3/2\,[7/2]_{3}$–$6p\,3/2\,[5/2]_{2}$
1010.827	100	98 928.87	$5d\,3/2\,[5/2]_{3}$–$6p\,3/2\,[3/2]_{2}$
1024.151	60	97 641.84	$5d\,3/2\,[5/2]_{2}$–$6p\,3/2\,[5/2]_{2}$
1043.576	6	95 824.32	$5d\,3/2\,[5/2]_{2}$–$6p\,3/2\,[1/2]_{1}$
1051.112	6	95 137.34	$5d\,3/2\,[3/2]_{1}$–$6p\,3/2\,[1/2]_{0}$
1051.438	4	95 107.83	$5d\,3/2\,[5/2]_{3}$–$6p\,3/2\,[5/2]_{3}$
1114.848	10	89 698.33	$6p\,3/2\,[5/2]_{3}$–$6d\,1/2\,[5/2]_{3}$
1141.824	60	87 579.18	$4f\,3/2\,[3/2]_{2}$–$5d\,3/2\,[5/2]_{3}$
1150.225	70	86 939.53	$5d\,3/2\,[3/2]_{1}$–$6p\,3/2\,[3/2]_{1}$
1186.865	200	84 255.58	$4f\,3/2\,[9/2]_{4}$–$5d\,3/2\,[5/2]_{3}$
1205.859	300	82 928.45	$4f\,3/2\,[5/2]_{3}$–$5d\,3/2\,[5/2]_{3}$
1211.818	250	82 520.65	$4f\,3/2\,[5/2]_{2}$–$5d\,3/2\,[3/2]_{1}$
1234.403	100	81 010.82	$4f\,3/2\,[3/2]_{2}$–$5d\,3/2\,[5/2]_{2}$
1250.718	4*p*	79 954.07	$4f\,3/2\,[7/2]_{3}$–$5d\,3/2\,[5/2]_{3}$
1264.429	80	79 087.08	$4f\,3/2\,[3/2]_{1}$–$5d\,3/2\,[3/2]_{2}$
1286.305	10	77 742.06	$4f\,1/2\,[5/2]_{3}$–$5d\,1/2\,[5/2]_{3}$
1299.297	150	76 964.70	$4f\,1/2\,[7/2]_{4}$–$5d\,1/2\,[5/2]_{3}$
1309.589	200	76 359.81	$4f\,3/2\,[5/2]_{3}$–$5d\,3/2\,[5/2]_{2}$
1315.354	800	76 025.14	$4f\,3/2\,[3/2]_{2}$–$5d\,3/2\,[3/2]_{2}$
1315.826	800	75 997.90	$4f\,3/2\,[7/2]_{4}$–$5d\,3/2\,[5/2]_{3}$
1331.550	800	75 100.46	$4f\,1/2\,[5/2]_{3}$–$5d\,1/2\,[3/2]_{2}$
1341.640	800*p*	74 535.63	$4f\,3/2\,[9/2]_{4}$–$5d\,3/2\,[7/2]_{3}$
1356.192	600	73 735.85	$4f\,3/2\,[3/2]_{1}$–$5d\,3/2\,[1/2]_{1}$
1358.358	700	73 618.27	$4f\,1/2\,[7/2]_{3}$–$5d\,1/2\,[5/2]_{2}$
1360.331	400	73 511.50	$4f\,3/2\,[9/2]_{4}$–$5d\,3/2\,[7/2]_{4}$
1360.786	200	73 486.94	$4f\,3/2\,[5/2]_{2}$–$5d\,3/2\,[5/2]_{3}$
1362.125	1000*p*	73 414.70	$4f\,3/2\,[9/2]_{5}$–$5d\,3/2\,[7/2]_{4}$
1362.463	200*p*	73 396.47	$6s\,3/2\,[3/2]_{2}$–$6p\,1/2\,[1/2]_{1}$
1362.668	800	73 385.44	$4f\,3/2\,[7/2]_{3}$–$5d\,3/2\,[5/2]_{2}$
1365.964	400	73 208.35	$4f\,3/2\,[5/2]_{3}$–$5d\,3/2\,[7/2]_{3}$
1385.346	400*p*	72 184.13	$4f\,3/2\,[5/2]_{3}$–$5d\,3/2\,[7/2]_{4}$
1401.064	950	71 374.34	$4f\,3/2\,[5/2]_{3}$–$5d\,3/2\,[3/2]_{2}$
1401.241	150*p*	71 365.33	$5d\,1/2\,[3/2]_{1}$–$6p\,1/2\,[1/2]_{0}$
1409.195	600	70 962.50	$4f\,3/2\,[3/2]_{1}$–$5d\,3/2\,[1/2]_{0}$
1414.959	800	70 673.42	$4f\,3/2\,[3/2]_{2}$–$5d\,3/2\,[1/2]_{1}$
1415.046	100*p*	70 669.10	$6p\,1/2\,[3/2]_{1}$–$6d\,1/2\,[3/2]_{1}$
1423.824	450	70 233.40	$4f\,3/2\,[7/2]_{3}$–$5d\,3/2\,[7/2]_{3}$
1444.901	200	69 208.89	$4f\,3/2\,[7/2]_{3}$–$5d\,3/2\,[7/2]_{4}$
1457.288	60	68 620.60	$6p\,1/2\,[3/2]_{1}$–$6d\,1/2\,[3/2]_{2}$
1459.172	60	68 532.01	$6p\,1/2\,[3/2]_{1}$–$6d\,1/2\,[5/2]_{2}$
1473.624	100	67 859.94	$6p\,3/2\,[5/2]_{2}$–$6d\,3/2\,[5/2]_{2}$
1475.078	200	67 793.03	$6p\,3/2\,[1/2]_{1}$–$6d\,3/2\,[3/2]_{2}$
1487.498	80	67 226.98	$6p\,3/2\,[3/2]_{1}$–$6d\,3/2\,[3/2]_{1}$
1494.356	550	66 918.47	$4f\,3/2\,[5/2]_{2}$–$5d\,3/2\,[5/2]_{2}$
1507.607	150	66 330.30	$6p\,3/2\,[5/2]_{2}$–$6d\,3/2\,[7/2]_{3}$
1508.812	350	66 277.31	$4f\,3/2\,[7/2]_{4}$–$5d\,3/2\,[7/2]_{3}$
1518.101	100	65 871.78	$6p\,3/2\,[1/2]_{1}$–$6d\,3/2\,[1/2]_{1}$
1532.497	650	65 252.98	$4f\,3/2\,[7/2]_{4}$–$5d\,3/2\,[7/2]_{4}$
1540.573	100*p*	64 910.92	$6p\,3/2\,[1/2]_{1}$–$6d\,3/2[1/2]_{0}$
1549.367	300	64 542.47	$6p\,3/2\,[5/2]_{3}$–$6d\,3/2\,[5/2]_{3}$
1568.225	350*p*	63 766.35	$4f\,3/2\,[5/2]_{2}$–$5d\,3/2\,[7/2]_{3}$
1575.641	300	63 466.25	$4f\,1/2\,[5/2]_{2}$–$5d\,3/2\,[3/2]_{1}$
1588.325	150*b*	62 959.41	$6p\,3/2\,[3/2]_{1}$–$6d\,3/2\,[5/2]_{2}$
1599.641	60	62 514.03	$6p\,1/2\,[3/2]_{2}$–$6d\,1/2\,[5/2]_{3}$
1605.239	100	62 296.01	$6p\,3/2\,[5/2]_{3}$–$6d\,3/2\,[7/2]_{3}$
1608.160	200	62 182.88	$6p\,3/2\,[5/2]_{3}$–$6d\,3/2\,[7/2]_{4}$
1610.488	30	62 092.97	$6p\,1/2\,[1/2]_{0}$–$6d\,1/2\,[3/2]_{1}$
1621.270	40	61 680.05	$6p\,1/2\,[1/2]_{1}$–$6d\,1/2\,[3/2]_{2}$
1628.460	20	61 407.73	$6p\,1/2\,[3/2]_{2}$–$6d\,1/2\,[5/2]_{2}$
1646.859	150	60 721.64	$6p\,3/2\,[3/2]_{2}$–$6d\,3/2\,[5/2]_{3}$
1694.062	60	59 029.70	$6p\,3/2\,[1/2]_{0}$–$6d\,3/2\,[3/2]_{1}$
1720.590	300	58 119.61	$6p\,3/2\,[3/2]_{2}$–$6d\,3/2\,[3/2]_{2}$
1741.233	150	57 430.58	$4f\,1/2\,[5/2]_{3}$–$5d\,3/2\,[5/2]_{3}$
1765.111	350	56 653.66	$4f\,1/2\,[7/2]_{4}$–$5d\,3/2\,[5/2]_{3}$
1767.382	150	56 580.85	$4f\,3/2\,[5/2]_{2}$–$5d\,3/2\,[1/2]_{1}$
1779.403	60	56 198.62	$6p\,3/2\,[3/2]_{2}$–$6d\,3/2\,[1/2]_{1}$
1824.990	200	54 794.82	$6s\,3/2\,[3/2]_{1}$–$6p\,3/2\,[1/2]_{0}$
1841.673	400	54 298.46	$4f\,1/2\,[7/2]_{3}$–$5d\,3/2\,[5/2]_{2}$
1955.172	350	51 146.40	$4f\,1/2\,[7/2]_{3}$–$5d\,3/2\,[7/2]_{3}$
1991.325	400	50 217.82	$6s\,3/2\,[3/2]_{2}$–$6p\,3/2\,[3/2]_{2}$
2018.054	450	49 552.68	$6s\,3/2\,[3/2]_{1}$–$6p\,3/2\,[3/2]_{2}$
2070.845	100	48 289.46	$6s\,1/2\,[1/2]_{1}$–$6p\,1/2\,[1/2]_{0}$
2081.251	60	48 048.03	$6s\,1/2\,[1/2]_{0}$–$6p\,1/2\,[1/2]_{1}$
2095.999	400	47 709.95	$4f\,1/2\,[5/2]_{3}$–$5d\,3/2\,[7/2]_{3}$
2115.855	20	47 262.22	$6s\,3/2\,[3/2]_{2}$–$6p\,3/2\,[3/2]_{1}$
2130.691	450	46 933.13	$4f\,1/2\,[7/2]_{4}$–$5d\,3/2\,[7/2]_{3}$
2135.022	250	46 837.92	$6s\,1/2\,[1/2]_{1}$–$6p\,1/2\,[3/2]_{2}$
2141.969	200	46 686.01	$4f\,1/2\,[5/2]_{3}$–$5d\,3/2\,[7/2]_{4}$
2143.434	200	46 654.10	$6s\,1/2\,[1/2]_{1}$–$6p\,1/2\,[1/2]_{1}$
2146.057	800*p*	46 597.09	$6s\,3/2\,[3/2]_{1}$–$6p\,3/2\,[3/2]_{1}$
2155.318	750*p*	46 396.87	$6s\,3/2\,[3/2]_{2}$–$6p\,3/2\,[5/2]_{3}$
2178.222	600	45 909.00	$4f\,1/2\,[7/2]_{4}$–$5d\,3/2\,[7/2]_{4}$
2360.591	650	43 362.27	$6s\,3/2\,[3/2]_{2}$–$6p\,3/2\,[5/2]_{2}$
2398.256	400*p*	41 696.96	$6s\,3/2\,[3/2]_{1}$–$6p\,3/2\,[5/2]_{2}$
2432.642	150	41 107.57	$6s\,1/2\,[1/2]_{0}$–$6p\,1/2\,[3/2]_{1}$
2466.420	800*p*	40 544.59	$6s\,3/2\,[3/2]_{2}$–$6p\,3/2\,[1/2]_{1}$
2518.038	300*p*	39 713.45	$6s\,1/2\,[1/2]_{1}$–$6p\,1/2\,[3/2]_{1}$

[a] Symbols: *p*, perturbed; *b*, blended.

[b] Wavelength and intensity from Reader and Ekberg, Ref. 5.

[c] Wavelengths from measurements in third and fourth orders of present observations; intensity from Reader and Ekberg, Ref. 5.

The wavelengths, intensities, and wave numbers of the classified lines of Ce V are given in Table I. All wavelengths are in vacuum. The estimated uncertainty of the wavelengths is ±0.005 Å. The intensities are visual estimates of plate blackening.

SPECTRUM ANALYSIS AND ENERGY LEVELS

The analysis of the spectrum was based almost entirely on the use of recurring wave-number intervals to establish the levels. Because of the rapidly changing structure of xenonlike ions and the fact that not all $5p^54f$ levels are known in La IV, only limited use could be made of isoelectronic graphs displaying the difference between observed and calculated wave numbers. Possible perturbation of the $5p^5nl$ configurations by the doubly excited configuration $5p^44f^2$ and by core-excited configurations of the type $5s5p^6nl$ added to the difficulty of using isoelectronic comparisons. Although transitions from the core-excited configurations $5s5p^64f$ and $5s5p^65d$ to $5s^25p^54f$ and $5s^25p^55d$ are expected to be strong, they lie outside our present region of observation.

Except for the line at 365.661 Å, the resonance transitions given by Reader and Ekberg[5] were all present in higher orders in our spectrograms. They could thus be measured to improved accuracy and used as a firm basis for extending the analysis. We first undertook analysis of the $5p^56s$-$6p$ transition array, which was expected to consist of a number of strong lines with predictable wavelengths. However, when this did not yield positive results the array was extended to include $5p^55d$-$6p$ transitions. With this extended array, all levels of the $5p^55d$, $6s$, and $6p$ configurations could be established. The $5p^55d$ levels were later confirmed by transitions to $5p^54f$, all of whose levels could also be established. The levels of $5p^56d$ were determined through transitions to $5p^56p$. Efforts to locate levels of $5p^57s$ by means of transitions to $5p^56p$ were unsuccessful. Apparently, $5p^56p$-$7s$ transitions are not present in our spectra.

The experimental energy levels for Ce V are given in Table II. The level values were determined by the computer code ELCALC,[9] which uses an iterative procedure to minimize the differences between observed and calculated wave numbers. The uncertainties are those determined by the code. The levels are designated in pair-coupling notation. The eigenvector compositions resulting from least-squares fits described below are also given in the table.

A few levels are determined by only one or two transitions. These levels are well supported by the calculations and the isoelectronic trends. There is little doubt as to their reality. Transitions involving levels based on the upper parent state $5p^5\,{}^2P_{1/2}$ were generally much weaker than those involving levels based on $5p^5\,{}^2P_{3/2}$. Evidently levels based on $5p^5\,{}^2P_{1/2}$ are relatively underpopulated in the spark.

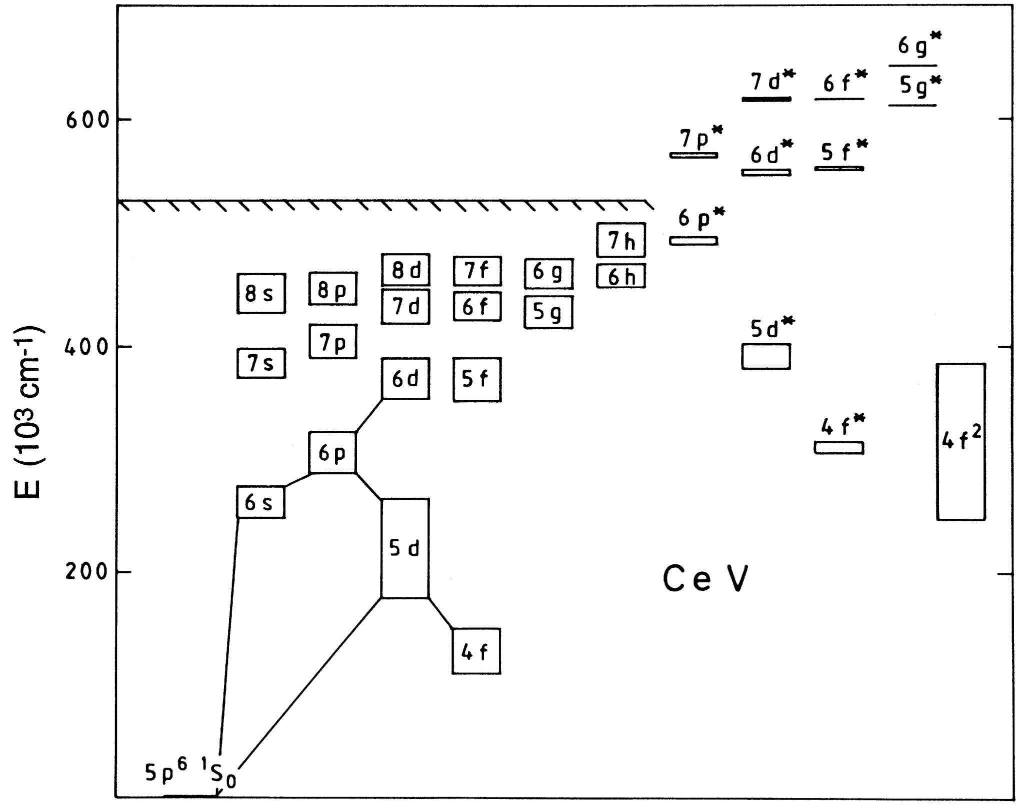

FIG. 2. The schematic diagram of predicted configurations of Ce V. Configurations between which transitions have been identified are joined by lines. Configurations noted as nl^* are of the type $5s5p^6nl$. The configuration noted as $4f^2$ represents $5p^44f^2$.

TABLE II. Experimentally determined energy levels (in cm^{-1}) and eigenvector compositions for Ce V.

Configuration	Term	J	Energy	Uncertainty	Leading eigenvector components		Percent LS coupling
$5p^6$	^1S	0	0.0	0.3			100% ^1S
$5p^54f$	3/2 [3/2]	1	107 397.7	0.2	100% 3/2 [3/2]		100% ^3D
	[3/2]	2	110 442.0	0.2	63% 3/2 [3/2]	33% 3/2 [5/2]	90% ^3D
	[9/2]	4	113 765.4	0.2	90% 3/2 [9/2]	9% 3/2 [7/2]	68% ^3G
	[9/2]	5	113 862.1	0.5	100% 3/2 [9/2]		100% ^3G
	[5/2]	3	115 092.7	0.2	87% 3/2 [5/2]	8% 1/2 [5/2]	68 ^3D
	[7/2]	3	118 067.4	0.2	89% 3/2 [7/2]	5% 1/2 [7/2]	45% ^3G
	[7/2]	4	122 023.6	0.2	89% 3/2 [7/2]	10% 3/2 [9/2]	58% ^3F
	[5/2]	2	124 534.4	0.1	67% 3/2 [5/2]	31% 3/2 [3/2]	49% ^1D
	1/2 [7/2]	3	137 154.4	0.1	94% 1/2 [7/2]	6% 3/2 [7/2]	52% ^3G
	[5/2]	3	140 590.8	0.1	91% 1/2 [5/2]	8% 3/2 [5/2]	45% ^3F
	[7/2]	4	141 367.7	0.1	97% 1/2 [7/2]	2% 3/2 [7/2]	39% ^3F
	[5/2]	2	143 588.9	0.3	95% 1/2 [5/2]	5% 3/2 [3/2]	50% ^1D
$5p^55d$	3/2 [1/2]	0	178 342.1	0.3	100% 3/2 [1/2]		100% ^3P
	[1/2]	1	181 115.3	0.1	64% 3/2 [1/2]	32% 3/2 [3/2]	92% ^3P
	[3/2]	2	186 467.0	0.2	88% 3/2 [3/2]	8% 1/2 [3/2]	74% ^3P
	[7/2]	4	187 276.8	0.1	100% 3/2 [7/2]		100% ^3F
	[7/2]	3	188 300.8	0.1	77% 3/2 [7/2]	20% 3/2 [5/2]	73% ^3F
	[5/2]	2	191 452.8	0.1	91% 3/2 [5/2]	5% 1/2 [5/2]	42% ^3F
	[5/2]	3	198 021.3	0.1	80% 3/2 [5/2]	20% 3/2 [7/2]	63% ^3D
	[3/2]	1	207 055.1	0.2	47% 3/2 [3/2]	42% 1/2 [3/2]	88% ^3D
	1/2 [5/2]	2	210 772.8	0.3	94% 1/2 [5/2]	5% 3/2 [5/2]	56% ^3F
	[3/2]	2	215 691.4	0.3	90% 1/2 [3/2]	8% 3/2 [3/2]	52% ^3D
	[5/2]	3	218 332.5	0.2	96% 1/2 [5/2]	3% 3/2 [7/2]	46% ^1F
	[3/2]	1	250 399.2	0.4	53% 1/2 [3/2]	24% 3/2 [1/2]	91% ^1P
$5p^56s$	3/2 [3/2]	2	246 732.3	0.1	99% 3/2 [3/2]		99% ^3P
	[3/2]	1	247 397.5	0.1	99% 3/2 [3/2]		63% ^1P
	1/2 [1/2]	0	272 080.9	0.1	100% 1/2 [1/2]		100% ^3P
	[1/2]	1	273 474.9	0.1	100% 1/2 [1/2]		63% ^3P
$5p^56p$	3/2 [1/2]	1	287 276.9	0.1	78% 3/2 [1/2]	22% 3/2 [3/2]	60% ^3S
	[5/2]	2	289 094.5	0.1	77% 3/2 [5/2]	23% 3/2 [3/2]	55% ^3D
	[5/2]	3	293 129.1	0.1	100% 3/2 [5/2]		100% ^3D
	[3/2]	1	293 994.6	0.1	78% 3/2 [3/2]	21% 3/2 [1/2]	58% ^1P
	[3/2]	2	296 950.1	0.1	77% 3/2 [3/2]	23% 3/2 [5/2]	65% ^3P
	[1/2]	0	302 192.2	0.2	90% 3/2 [1/2]	10% 1/2 [1/2]	64% ^3P
	1/2 [3/2]	1	313 188.4	0.1	90% 1/2 [3/2]	10% 1/2 [1/2]	71% ^3D
	[1/2]	1	320 129.0	0.1	89% 1/2 [1/2]	10% 1/2 [3/2]	57% ^3P
	[3/2]	2	320 312.8	0.1	100% 1/2 [3/2]		45% ^3D
	[1/2]	0	321 764.4	0.1	90% 1/2 [1/2]	10% 3/2 [1/2]	64% ^1S
$5p^56d$	3/2 [1/2]	0	352 187.8	0.4	100% 3/2 [1/2]		100% ^3P
	[1/2]	1	353 148.7	0.1	66% 3/2 [1/2]	34% 3/2 [3/2]	86% ^3P
	[3/2]	2	355 069.8	0.2	96% 3/2 [3/2]	3% 3/2 [5/2]	58% ^3P
	[7/2]	4	355 312.0	0.2	100% 3/2 [7/2]		100% ^3F
	[7/2]	3	355 425.0	0.2	90% 3/2 [7/2]	10% 3/2 [5/2]	59% ^3F
	[5/2]	2	356 954.4	0.2	96% 3/2 [5/2]	3% 3/2 [3/2]	52% ^1D
	[5/2]	3	357 671.7	0.2	90% 3/2 [5/2]	10% 3/2 [7/2]	68% ^3D
	[3/2]	1	361 221.8	0.2	65% 3/2 [3/2]	32% 3/2 [1/2]	54% ^1P
	1/2 [5/2]	2	381 720.5	0.2	97% 1/2 [5/2]	2% 1/2 [3/2]	71% ^3F
	[3/2]	2	381 809.0	0.2	97% 1/2 [3/2]	2% 1/2 [5/2]	41% ^3D
	[5/2]	3	382 826.9	0.2	100% 1/2 [5/2]		39% ^3F
	[3/2]	1	383 857.4	0.2	98% 1/2 [3/2]		46% ^3D

THEORETICAL INTERPRETATION AND DISCUSSION

Figure 2 shows the predicted positions of the primary configurations of Ce v. The predictions were made with the relativistic Hartree-Fock (HF) code of Cowan.[10] The level structures of the experimentally observed configurations are shown in Fig. 3. The levels are designated in pair coupling, with the K value noted for each pair. As can be seen, the coupling deviates significantly from pure pair coupling for the observed configurations.

The levels were interpreted by first making an *ab initio* calculation of the energy parameters for all configurations in Fig. 2 with the Cowan code.[10] The code was run in the Hartree-Fock relativistic (HFR) mode with no scaling of the parameters. In this mode the relativistic mass correction and the Darwin term are included in the self-consistent-field calculation of the radial part of the wave function. This results in a relativistic contraction of the electron orbitals, which must be present in the calculation in order to obtain realistic values of the energy parameters. The radial part of the wave function was optimized individually for each configuration without keeping the core frozen.

After the energy levels were established, the energy parameters were fit to the levels by the least-squares fitting routine of the Cowan code. Only experimentally observed configurations were included in the least-squares calculations. The fitted values of the parameters are compared with the HF values in Table III. The leading eigenvector percentages for each level are given in Table II.

The deviations from pure pair coupling seen in Fig. 3 and the low pair-coupling percentages in Table II are the result of large electrostatic exchange interactions between the $5p^5$ core electrons and the valence electron. For a configuration such as $5p^54f$ these interactions are usually small and the coupling nearly pure pair coupling. However, collapse of the $4f$ orbital causes increased electrostatic interaction between the $5p$ and $4f$ electrons, with the consequent deviation from pure pair coupling for the

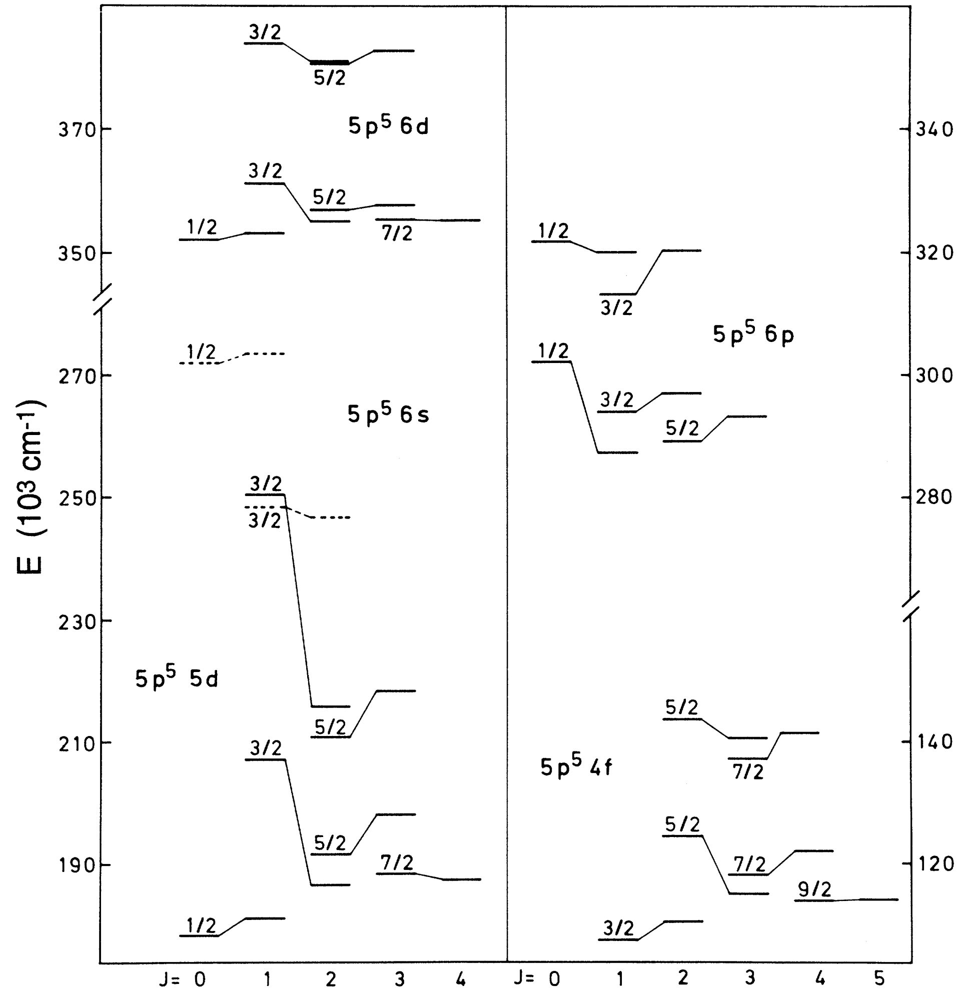

FIG. 3. Level structures of the observed configurations of Ce v. Levels belonging to $5p^56s$ are shown as dashed lines. Levels are designated in pair coupling with the K value indicated for each pair. The J value of the core is not shown.

TABLE III. Energy parameters in cm^{-1} and mean errors Δ of least-squares fits for Ce V.

Configuration	Parameter	HF	Fitted	Ratio of fitted value to HF value
$5p^6$	E_{av}	0	515±331	
$5p^5 4f$	E_{av}	130 406	124 248±98	
	$F^2(5p4f)$	51 785	38 322±1540	0.74
	$G^2(5p4f)$	28 093	24 289±767	0.86
	$G^4(5p4f)$	21 746	21 114±2440	0.97
	ζ_{5p}	15 379	14 996±175	0.98
	ζ_{4f}	729	712±75	0.98
$5p^5 6p$	E_{av}	304 036	301 431±113	
	$F^2(5p6p)$	20 415	12 009±1743	0.59
	$G^0(5p6p)$	3 664	3 112±105	0.85
	$G^2(5p6p)$	5 232	7 611±1556	1.45
	ζ_{5p}	17 111	16 911±154	0.99
	ζ_{6p}	3 396	3 938±192	1.16
$5p^6$-$5p^5 4f$	$R^2(5p5p,5p4f)$	−37 911	−37 911[a]	
$5p^6$-$5p^5 6p$	$R^0(5p5p,5p6p)$	1 699	1 699[a]	
	$R^2(5p5p,5p6p)$	8 264	8 264[a]	
$5p^5 6p$-$5p^5 4f$	$R^2(5p6p,5p4f)$	−7 866	−7 866[a]	
	$R^2(5p6p,4f5p)$	−5 013	−5 013[a]	
Mean error	Δ	330		
$5p^5 5d$	E_{av}	203 298	200 895±132	
	$F^2(5p5d)$	52 878	39 672±1350	0.75
	$G^1(5p5d)$	62 695	48 218±438	0.77
	$G^3(5p5d)$	39 474	31 723±2482	0.80
	ζ_{5p}	16 502	15 754±248	0.95
	ζ_{5d}	1169	1319±151	1.13
$5p^5 6s$	E_{av}	258 608	255 513±231	
	$G^1(5p6s)$	6 810	2 860±1263	0.42
	ζ_{5p}	16 962	17 381±301	1.02
$5p^5 6d$	E_{av}	367 499	364 576±133	
	$F^2(5p6d)$	14 374	13 717±1616	0.95
	$G^1(5p6d)$	8 107	3 901±546	0.48
	$G^3(5p6d)$	5 882	6 727±2557	1.14
	ζ_{5p}	17 102	17 402±188	1.02
	ζ_{6d}	318	319±129	1.00
$5p^5 5d$–$5p^5 6s$	$R^2(5p5d,5p6s)$	−12 336	−12 336[a]	
	$R^1(5p5d,6s5p)$	−4 434	−4 434[a]	
$5p^5 5d$–$5p^5 6d$	$R^2(5p5d,5p6d)$	14 036	14 036[a]	
	$R^1(5p5d,6d5p)$	20 652	20 652[a]	
	$R^3(5p5d,6d5p)$	13 690	13 690[a]	
$5p^5 6d$–$5p^5 6s$	$R^2(5p6d,5p6s)$	9 178	9 178[a]	
	$R^1(5p6d,6s5p)$	1 217	1 217[a]	
Mean error	Δ	435		

[a] Fixed at HF value.

$5p^54f$ configuration.

As seen in Fig. 3 the $5p^56s\ 3/2[3/2]_1$ and $5p^55d\ 1/2[3/2]_1$ levels have nearly the same energies. In principal these levels should interact strongly because each has significant ^1P character. According to the eigenvectors calculated with the fitted parameter values the $5p^56s$ level has 63% ^1P character and the $5p^55d$ level 91% ^1P character. However, as seen in Table II there is almost no admixture of configurations for these levels. The complete eigenvectors indicate an admixture of only about 0.4%. This low level of mixing is confirmed by the absence of $5p^56s\ 3/2[3/2]_1$–$5p^54f$ transitions in the observed spectrum. This is also suggested by the isoelectronic curves of Reader and Epstein,[11] which show these two levels to cross in Ce v with no apparent perturbation. This unusual absence of perturbation is attributable to the fact that the coefficients of $R^2(5p5d,5p6s)$ and $R^1(5p5d,6s5p)$ in the matrix element for the ^1P-^1P interaction have opposite signs, producing an almost complete cancellation of the interaction for the present values of the parameters. (The ^1P-^1P matrix element is given by $2^{1/2}[R^2(5pd,5p6s)/5\text{-}2R^1(5p5d,6s5p)/3]$.)

Some of the ratios of the fitted to HF values in Table III differ significantly from unity, most notably $F^2(5p6p)$, $G^2(5p6p)$, $G^1(5p6s)$, and $G^1(5p6d)$. This is probably due to perturbations by core-excited configurations. configurations.

In Fig. 4 we plot the radial wave functions calculated with the Cowan code for the $4f$ electron of the $5p^54f$ configuration in the first five ions of the xenon isoelectronic sequence. As described by Goeppert Mayer,[6] the collapse of the $4f$ shell is caused by a deepening of an inner well in the effective potential for f electrons to the point that a bound state can exist in the inner region. The wave function for Xe, shown in Fig. 4, is practically hydrogenic. The wave function for Cs II is nearly hydrogenic, but has some increased amplitude in the inner region, even though the inner well is not deep enough to support a bound state. In Ba III the $4f$ wave function is almost fully collapsed. In La IV and Ce v the $4f$ wave functions are fully collapsed. The appearance of these wave functions closely resembles those calculated by Lucatorto *et al.*[12] and Cheng and Froese Fischer[13] for the $4f$ electron in the $4d^94f5s^25p^6$ configurations of Xe-like ions.

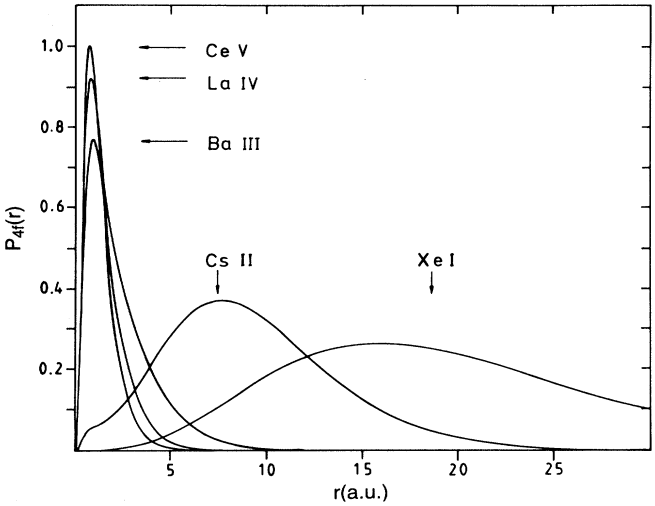

FIG. 4. Configuration-average radial wave functions for the $4f$ electron of the $5p^54f$ configuration in xenonlike ions from Xe I to Ce v.

IONIZATION ENERGY

In Ref. 11 an ionization energy for Ce v of 528 700±2000 cm^{-1} was derived by using extrapolated values for the $J=1$ levels of $5p^57s$ and an assumed value is 1.050±0.005 for the change in quantum defect between the $5p^56s$ and $5p^57s$ configurations, $\Delta n^*(7s\text{-}6s)$. With our present data for the $5p^55d$ and $5p^56d$ configurations we are able to obtain a second value for this ionization energy. Considering only the $J=4$ levels of these two configurations we find $\Delta n^*(6d-5d)=1.15475(3)$ for Cs II (Ref. 2), 1.1884(6) for Ba III (Ref. 3), and 1.164(9) for La IV (Ref. 4). Assuming $\Delta n^*=1.17(2)$ for Ce v, we obtain a limit of 525 100±2600 cm^{-1}. For the ionization energy we adopt a weighted average of the two vlaues, 527 100±2000 cm^{-1} (65.35±0.25 eV).

ACKNOWLEDGMENTS

We thank N. Acquista for assistance in photographing the spectra at NIST. The work at NIST was supported in part by the Office of Fusion Energy of the U. S. Department of Energy. Andreas Redfors is grateful for support from Kungliga Fysiografiska Sällskapet i Lund and for the hospitality of the staff at NIST during his visit there.

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