

Observation of inner-shell-excited configurations in triply ionized cerium Ce³⁺

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We report wavelength measurements and energy levels for the three-times ionized cerium atom Ce³⁺. The spectrum is that of a simple one-electron atom overlaid with a more complex three-electron spectrum originating from the excitation of an electron in the inner closed shell to the valence shell. The data provide energy levels for the inner-shell-excited configurations $5p^54f5d$ and $5p^54f6s$ and solve a long-standing puzzle regarding the fine structure of the $5p^66d$ configuration, which is known to be anomalously large and inverted. The data show that this anomalous fine structure is the result of interaction between $5p^66d$ and the inner-shell-excited configuration $5p^54f5d$. The results are supported by Hartree-Fock calculations and least-squares fits of the energy parameters to the observed levels. From our observed $5p^66g$ configuration, we determine the ionization energy as $297670 \pm 70 \text{ cm}^{-1}$ ($36.906 \pm 0.009 \text{ eV}$).

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I. INTRODUCTION

As a member of the cesium isoelectronic sequence, the Ce³⁺ ion is expected to have a simple electronic structure, with a single valence electron outside a complete $5p^6$ subshell. In large measure, this is indeed the case. Ce³⁺ has ground configuration $5p^64f$ and excited states of the type $5p^6nl$. The first classified lines in the spectrum, the $6s$ - $6p$ doublet, were given by Gibbs and White [1]. The first set of energy levels, with $5p^65d$ as the ground configuration, was given by Lang [2]. Nevertheless, Lang realized that until the $4f$ - $5d$ multiplet was located, there was a possibility that the true ground state could be $5p^64f$. A short time later, Lang [3,4] succeeded in locating the $4f$ - $5d$ multiplet and, indeed, established $5p^64f$ as the ground configuration. This established Ce³⁺ as a true rare-earth-metal atom in the sense of its having a $4f$ electron in the ground state. The $6d^2D$ term found by Lang was puzzling in that it was inverted and had a very large fine-structure splitting. As mentioned in the compilation of the energy levels of Ce³⁺ by Martin *et al.* [5], it was suggested by one of us (J.R.) that this anomalous splitting was due to interaction with inner-shell-excited configurations.

The purpose of our present work was to re-examine Lang's analysis of this ion, determine explicitly the reason for the anomalous splitting of the $6d^2D$ term, and locate levels of some of the inner-shell-excited configurations.

II. EXPERIMENT

The spectra were photographed with the 10.7-m normal-incidence vacuum spectrograph at the National Institute of Standards and Technology (NIST). A gold grating with 1200 lines/mm was used to observe the region 400–950 Å. The light source was a low-voltage sliding spark between metallic cerium electrodes operated as described by Reader *et al.* [6]. The plate factor was 0.78 Å/mm. Ionization stages were determined by comparing intensities of the lines at various

peak currents in the spark. The spectrum of Ce³⁺ was effectively excited at a peak current of 140 A. Reference spectra consisted of lines of several stages of ionization of yttrium photographed on a separate track for the sliding spark [7–10]. Shifts between the calibration spectra and the unknown spectra were determined by lines of oxygen, carbon, and silicon, with wavelengths taken from Kelly and Palumbo [11]. For the region 950–3200 Å, we made use of spectra observed for the analysis of Ce⁴⁺ by Redfors and Reader [12].

The wavelengths, intensities, and wave numbers of the classified lines of Ce³⁺ are given in Table I. The estimated uncertainty of the wavelengths is $\pm 0.005 \text{ Å}$ [13]. The intensities are visual estimates of plate blackening (see Tauheed and Reader [14] for a description of this estimation process). For extremely strong lines with saturated images, the intensities were estimated by observing degrees of solarization and intensities of grating ghosts. No account was taken of spectral response of the spectrometers.

III. SPECTRUM ANALYSIS AND ENERGY LEVELS

Our interpretation of the spectrum was guided by calculations of the level structures and transition probabilities carried out with the atomic structure suite of codes of Cowan [15]. The Hartree-Fock code (RCN) was run in a Hartree-Fock relativistic (HFR) mode with a correlation term in the potential and with no Breit energies. Further guidance was obtained from a two-dimensional transition array with the computer spreadsheet method described by Reader [16]. Altogether, we determined 112 energy levels from 200 observed lines.

Our analysis confirmed the $4f$, $5d$, $5f$, $6s$, $6p$, $6d$, $7s$, and $7d_{3/2}$ levels of Lang. We found Lang's $5g$, $6g$, $7d_{5/2}$, and $8s$ levels to be spurious. Lang's $6g$ level had earlier been discarded by Martin *et al.* [5]. We located numerous levels of the inner-shell-excited configurations $5p^54f5d$ and $5p^54f6s$ as well as the $7p$ and $8d$ levels and determined new values for the $5g$, $6g$, and $7d_{5/2}$ levels.

TABLE I. Observed spectral lines of Ce^{3+} . All wavelengths are in vacuum. Level codes are explained in text. Numbers in brackets denote powers of 10.

Wavelength (Å)	Intensity	Odd Level	Even level	$\log g_L f$	$g_U A$ (s^{-1})
402.904	20	4f02	6g03	-0.76	7.13[9]
404.405	10	4f02	8d01	-0.85	5.75[9]
406.570	40	4f03	6g04	-0.57	1.08[10]
407.743	25	4f03	8d02	-0.65	9.01[9]
426.811	50	4f02	s207	-0.08	3.03[10]
427.385	40	4f02	s104	-0.07	3.08[10]
430.281	1	4f02	s307	-1.96	3.96[8]
430.954	5	4f03	s207	-1.01	3.49[9]
433.503	2	4f02	s206	-7.59	9.19[2]
434.495	90	4f03	s307	0.26	6.39[10]
436.017	150	4f03	s404	0.35	7.92[10]
436.288	5	4f02	d223	-0.47	1.19[10]
437.776	90	4f03	s206	0.50	1.10[11]
438.823	100	4f02	s305	0.33	7.38[10]
439.134	100	4f02	d119	0.80	2.17[11]
439.650	90	4f02	s205	-0.25	1.96[10]
440.621	100	4f03	d223	0.95	3.07[11]
440.975	40	4f02	5g03	0.26	6.22[10]
444.453	125	4f03	5g04	1.07	3.92[11]
444.605	100	4f02	d323	-1.20	2.15[9]
445.398	100	4f03	5g03	-0.12	2.58[10]
446.318	150	4f02	d222	1.11	4.31[11]
446.540	150	4f02	d322	1.20	5.33[11]
448.669	175	4f03	d419	1.02	3.48[11]
449.100	15	4f03	d323	1.25	5.87[11]
449.280	40	4f02	7d02	-0.17	2.25[10]
451.078	5	4f03	d322	-0.24	1.90[10]
451.138	150	4f02	7d01	0.49	1.01[11]
453.874	150	4f03	7d02	0.35	7.27[10]
465.911	50	4f02	s204	-0.72	5.94[9]
467.975	100	4f02	s103	-1.40	1.22[9]
470.852	200	4f03	s204	-0.33	1.41[10]
471.296	5	4f02	s304	-1.70	5.99[8]
475.345	100	4f02	d118	-0.63	6.92[9]
476.350	400	4f03	s304	-0.13	2.20[10]
478.080	400	4f03	s403	-0.39	1.20[10]
480.579	400	4f02	s303	-0.15	2.04[10]
481.454	300	4f02	s203	-0.53	8.55[9]
484.998	250	4f02	s202	-0.53	8.39[9]
485.361	400	4f03	d418	0.15	4.00[10]
485.837	50	4f03	s303	-1.07	2.43[9]
486.729	40	4f03	s203	-1.13	2.11[9]
488.793	500	4f02	s302	-0.44	1.03[10]
489.853	500	4f02	s301	-0.35	1.25[10]
490.354	400	4f03	s202	-0.36	1.22[10]
491.233	250	4f02	d321	-1.37	1.19[9]
492.183	350	4f02	d220	-0.98	2.91[9]

TABLE I. (*Continued.*)

Wavelength (Å)	Intensity	Odd Level	Even level	$\log g_L f$	$g_U A$ (s^{-1})
493.854	750	4f03	s402	-0.06	2.39[10]
494.233	250	4f03	s302	-1.43	1.02[9]
495.174	200	4f02	d320	-1.69	5.55[8]
495.317	25	4f03	s301	-1.17	1.84[9]
496.730	350	4f03	d321	-0.61	6.71[9]
497.343	400	4f02	s102	-0.53	8.01[9]
497.699	50	4f03	d220	-1.18	1.80[9]
498.455	400	4f03	s401	-1.22	1.60[9]
499.581	350	4f02	d115	-0.36	1.16[10]
500.328	400	4f02	s201	-0.96	2.90[9]
500.765	150	4f03	d320	-1.14	1.91[9]
503.720	250	4f03	d417	-1.32	1.28[9]
505.262	350	4f02	d218	-2.53	7.64[7]
505.850	200	4f02	d319	-1.44	9.39[8]
506.029	400	4f03	s201	-1.51	8.13[8]
507.755	600	4f02	s101	-1.20	1.63[9]
508.501	400	4f02	d217	-0.48	8.63[9]
511.079	500 ^a	4f02	d318	-0.96	2.81[9]
511.079	500 ^a	4f03	d218	-1.93	2.97[8]
511.329	600	4f03	d416	-1.05	2.29[9]
511.680	500	4f03	d319	-1.25	1.43[9]
514.348	600	4f02	d216	-0.59	6.42[9]
514.389	400	4f03	d217	-0.42	9.48[9]
515.183	500	4f03	d415	-1.84	3.62[8]
517.029	50	4f03	d318	-2.47	8.39[7]
518.919	40	4f02	d215	-1.46	8.59[8]
520.896	600	4f02	d112	-0.32	1.19[10]
521.907	500	4f02	d316	-1.10	1.93[9]
522.650	550	4f03	d414	-4.81	3.83[5]
525.056	750	4f03	d215	-0.39	9.81[9]
528.115	500	4f03	d316	-1.00	2.37[9]
528.707	10 ^b	4f02	d315	-1.62	5.72[8]
529.444	1000	4f03	d413	0.03	2.56[10]
533.056	600	4f02	d214	-0.94	2.72[9]
534.345	750	4f02	d314	-0.11	1.79[10]
535.084	750	4f03	d315	-0.12	1.75[10]
536.832	750	4f03	d412	-0.86	3.18[9]
539.040	600	4f02	d213	-0.20	1.46[10]
539.532	100	4f03	d214	-2.02	2.18[8]
540.855	450	4f03	d314	-0.76	3.98[9]
541.645	1000	4f03	d411	-0.61	5.62[9]
542.600	375	4f02	d109	-2.05	2.02[8]
545.375	1000	4f02	d313	-0.75	4.00[9]
545.664	50	4f03	d213	-1.51	6.91[8]
545.868	550	4f02	d212	-1.31	1.11[9]
552.150	750 ^c	4f03	d313	-1.45	7.80[8]
552.665	500	4f03	d212	-1.22	1.32[9]
553.748	750	4f02	d312	-1.15	1.56[9]

TABLE I. (*Continued.*)

Wavelength (Å)	Intensity	Odd Level	Even level	$\log g_L f$	$g_U A$ (s^{-1})
555.133	50	4f02	d211	-3.28	1.14[7]
557.394	25	4f02	d210	-2.48	7.15[7]
558.932	500	4f02	6d01	-1.30	1.07[9]
560.742	750	4f03	d312	-1.28	1.11[9]
562.168	500	4f03	d211	-1.56	5.84[8]
562.501	1250	4f02	d311	-1.48	6.95[8]
564.338	200	4f02	6d02	-2.24	1.21[8]
565.209	750	4f03	d410	-2.24	1.20[8]
566.951	750	4f02	d310	-3.80	3.33[6]
569.004	750	4f02	d108	-1.14	1.49[9]
569.719	400	4f03	d311	-4.89	2.67[5]
571.004	875	4f02	d309	-1.47	6.95[8]
571.605	750	4f03	6d02	-1.09	1.67[9]
572.532	50	4f03	d409	-2.21	1.26[8]
573.279	1250	4f03	d408	-1.16	1.41[9]
573.566	200	4f02	d209	-2.04	1.85[8]
574.284	700	4f03	d310	-1.59	5.25[8]
575.051	25	4f02	d107	-4.12	1.52[6]
577.209	1000	4f02	d208	-0.99	2.04[9]
578.068	500	4f02	d106	-1.79	3.28[8]
578.444	500	4f03	d309	-1.43	7.40[8]
578.504	50	4f02	d308	-3.18	1.32[7]
581.073	1000	4f03	d209	-1.10	1.58[9]
582.216	400	4f02	d307	-5.12	1.48[5]
583.971	750	4f02	d105	-1.87	2.61[8]
584.166	500	4f02	d207	-1.79	3.19[8]
584.812	100	4f03	d208	-4.42	7.42[5]
584.625	600	4f03	d407	-2.02	1.87[8]
585.100	15	4f02	d306	-3.58	5.13[6]
586.143	1500	4f03	d308	-0.95	2.17[9]
589.166	150	4f02	d206	-2.49	6.21[7]
589.521	400	4f02	d305	-3.01	1.87[7]
589.951	375	4f03	d307	-1.68	4.01[8]
591.955	600	4f03	d207	-2.63	4.44[7]
592.915	250	4f03	d306	-3.45	6.78[6]
593.027	225	4f03	d405	-2.42	7.14[7]
593.447	600	4f02	d104	-2.70	3.83[7]
596.831	750	4f02	d205	-2.22	1.13[8]
597.090	1250	4f03	d206	-1.91	2.29[8]
597.460	1250	4f03	d305	-1.49	6.05[8]
601.448	450	4f02	d103	-2.98	1.94[7]
603.183	250	4f02	d304	-2.57	4.99[7]
604.964	125	4f03	d205	-4.27	9.87[5]
610.375	40	4f02	d303	-3.37	7.59[6]
610.472	1000	4f02	d204	-1.25	9.99[8]
611.488	1250	4f03	d304	-1.44	6.54[8]
613.145	250	4f02	d203	-2.65	4.01[7]
616.792	1000	4f02	d202	-1.65	3.93[8]

TABLE I. (*Continued.*)

Wavelength (Å)	Intensity	Odd Level	Even level	$\log g_L f$	$g_U A$ (s^{-1})
618.884	1250	4f03	d303	-1.64	3.98[8]
618.978	500	4f03	d204	-1.85	2.49[8]
620.298	750	4f03	d302	-1.71	3.40[8]
627.599	1250	4f03	d401	-1.84	2.48[8]
629.405	1250	4f02	d301	-1.93	1.97[8]
638.453	25	4f03	d301	-3.45	5.76[6]
671.033	250	7p00	5d01	-1.25	8.28[8]
671.304	500 ^d	7p01	5d02	-1.11	1.15[9]
741.808	75000	5f02	5d01	0.30	2.43[10]
754.608	125000	5f03	5d02	0.46	3.41[10]
755.760	10000	5f02	5d02	-0.85	1.65[9]
891.587	1000	7p00	6s01	-4.65	1.88[5]
1289.408	100	6p01	5d01	-0.90	5.07[8]
1332.157	5000	6p01	5d02	0.04	4.11[9]
1372.719	3500	6p00	5d01	-0.23	2.10[9]
1528.667	20	6p01	d215	-1.11	2.21[8]
1570.956	20	5f02	6g03	0.08	3.25[9]
1575.641	40	5f03	6g04	0.19	4.12[9]
1633.698	1000	6p00	d005	-1.41	9.70[7]
1641.591	5000	6p00	7s01	-0.36	1.07[9]
1717.489	5	6p01	d213	-2.76	3.94[6]
1769.788	150	6p01	d005	-1.13	1.58[8]
1775.304	25000	6p00	6d01	0.17	3.10[9]
1779.060	10000	6p01	7s01	-0.10	1.67[9]
1788.813	12000	6p01	d212	-0.36	9.12[8]
1881.067	20000	6p00	d108	-0.13	1.40[9]
1892.370	18000	6p01	d211	-0.49	6.04[8]
1914.740	60000	4f02	5d02	-2.19	1.16[7]
1918.842	30	6p01	d210	0.02	1.87[9]
1937.185	12000	6p01	6d01	-0.57	4.76[8]
1948.828	20000	6p00	d107	-0.55	4.94[8]
1983.919	9000	6p00	d106	-2.81	2.64[6]
2001.046	6000000	4f03	5d02	-0.92	2.00[8]
2003.726	40000	6p01	6d02	0.33	3.56[9]
2010.562	3000000	4f02	5d01	-1.08	1.37[8]
2055.214	9000	6p00	d105	-2.07	1.33[7]
2061.089	40	7p00	8d01	-0.70	3.11[8]
2063.796	15000	6p01	d108	-0.88	2.07[8]
2125.119	4000	6p01	d209	-1.54	4.25[7]
2145.654	30000	6p01	d107	-1.28	7.65[7]
2159.145	150	7p01	8d02	-0.49	4.58[8]
2175.994	40000	6p01	d208	-0.60	3.50[8]
2177.598	150	6p00	d104	-2.03	1.33[7]
2188.261	20	6p01	d106	-4.53	4.10[4]
2275.319	150	6p01	d105	-2.74	2.35[6]
2278.285	40000	6p01	d207	-1.40	5.18[7]
2289.380	140	6p00	d103	-2.78	2.11[6]
2352.703	200	5f03	5g04	0.71	6.16[9]

TABLE I. (Continued.)

Wavelength (Å)	Intensity	Odd Level	Even level	$\log g_L f$	$g_U A$ (s^{-1})
2368.060	200	5f02	5g03	0.83	8.07[9]
2379.435	5	5f03	5g03	-0.62	2.82[8]
2426.288	12	6p01	d104	-2.57	3.10[6]
2457.600	300000	6p01	6s01	0.23	1.88[9]
2475.908	200	5f03	d419	0.73	5.89[9]
2537.880	20	5f02	d322	-0.14	7.32[8]
2643.099	5	5f03	7d02	-0.69	1.96[8]
2779.075	100000	6p00	6s01	-0.12	6.50[8]
2870.443	5	6p01	d202	-3.44	2.96[5]
3020.413	10	7p01	s207	-1.97	7.84[6]

^aDoubly classified.

^bPerturbed by Ce^{4+} ; not included in level optimization.

^cPerturbed by Ce^{4+} .

^dPerturbed by N^+ .

Most of the levels of $5p^54f5d$ and $5p^54f6s$ are determined by pairs of lines that connect upper levels to the $4f^2F$ ground-state doublet. Many of these upper levels are confirmed by transitions to other $5p^6nl$ levels, mostly $6p$. Some of the predicted upper levels have J values that are too low or too high ($J < 3/2$ or $J > 9/2$) to make dipole-allowed transitions to $4f$. Levels with $J=1/2$ can make transitions to levels of $6p$ and $7p$, and we established one level of $5p^54f5d$ through its transitions to $6p$. The levels with $J=3/2$ and $9/2$ are mostly established by a single transition each. These are generally strong lines that are easily identified in the spectrum. Some of the $J=3/2$ levels are confirmed by transitions to $6p$.

As shown in Table I, one line, 511.079 Å, is doubly classified. The $5d_{3/2}-7p_{3/2}$ transition, which is expected to lie at 660.274 Å, is evidently masked by a strong line of singly ionized nitrogen at 660.286 Å [11]. Our line at 1575.641 Å is also given in the list of lines for Ce^{4+} [12]. However, according to our present assessment, it clearly belongs to Ce^{3+} .

The experimental energy levels for Ce^{3+} are given in Table II. The level values were determined by the computer code ELCALC [17], which uses an iterative procedure to minimize the differences between observed and calculated wave numbers. The uncertainties are those determined by the code. The designations for the $5p^6nl$ levels are given as the configuration followed by the truncated J value ($4f02$ indicates $5p^64f$ with J value of 2.5). For the $5p^54f5d$ and $5p^54f6s$ configurations, the designations are given as configuration, followed by truncated J value, and followed by the ordinal number of the calculated level for this configuration and J value ($d419$ indicates the level calculated as the 19th level with $J=4.5$ in the configuration $5p^54f5d$; $s104$ indicates the 4th level with $J=1.5$ in the configuration $5p^54f6s$).

IV. RITZ WAVELENGTHS

We calculated wavelengths of selected observed lines determined by the optimized level values or Ritz values. The

results are given in Table A, which is available online in the electronic physics auxiliary publication service (EPAPS) of the American Institute of Physics [18]. The calculated wavelengths of these lines have especially low uncertainties. The uncertainties of the Ritz wavelengths correspond to the square root of the sum of the squares of the uncertainties of the combining levels. The Ritz wavelengths have uncertainties as low as 0.0003 Å. Comparison of the observed wavelengths with the Ritz wavelengths shows that our estimate of 0.005 Å for the general wavelength uncertainty is fully justified.

To a large extent, the low uncertainties for the Ritz wavelengths arise from the observation of long-wavelength transitions between one-electron configurations and the inner-shell excitation configurations that take place because of configuration interaction. Fig. 1 shows all the observed levels and illustrates the origin of the low uncertainties for the Ritz wavelengths. There are two types of Ritz systems here. First, the $4f-5d$, $5d-6p$, and $6p-6d$ transitions combine to produce level values for $6d$ that are accurate to 0.12 cm^{-1} . Combined with the 0.13 cm^{-1} uncertainty of the $4f$ ground term, the wavelengths for the $4f-6d$ transitions are then accurate to $\pm 0.18 \text{ cm}^{-1}$ or $\pm 0.0006 \text{ Å}$. Second, the $4f-5d$, $5d-6p$, and $5p^66p-5p^54f5d$ transitions combine to produce levels of $5p^54f5d$ that are accurate to about 0.10 cm^{-1} . The transitions from these levels to the ground term are thus accurate to about $\pm 0.0006 \text{ Å}$. The $5p^66p-5p^54f5d$ transitions, which are not normally allowed as they would involve a change of two electrons, take place because of mixtures of $5p^54f5d$ levels with the $5p^66d$ levels. As mentioned, this is the cause of the abnormal fine structure of the $5p^66d$ levels found originally by Lang [4]. For both of these Ritz schemes, the uncertainty of the calculated wavelengths in large measure derives from the uncertainty of the shortest wavelength lines in the calculation, which for the present set is the group at 1300 Å.

TABLE II. Energy levels of Ce^{3+} in cm^{-1} . Percentage compositions are given in Table C [18]. Level codes are explained in text.

Config.	Term	J	Desig.	Energy	Unc.	Config. int.
$5p^64f$	2F	2.5	4f02	0.00	0.13	
		3.5	4f03	2252.50	0.16	
$5p^65d$	2D	1.5	5d01	49737.30	0.14	1% $5p^54f5d$
		2.5	5d02	52226.33	0.14	1% $5p^54f5d$
$5p^66s$	2S	0.5	6s01	86602.10	0.06	1% $5p^56p5d$
$5p^66p$	2P	0.5	6p00	122585.29	0.05	
		1.5	6p01	127292.24	0.04	
$5p^66d$	2D	2.5	6d02	177199.23	0.13	51% $5p^54f5d$
		1.5	6d01	178913.57	0.12	45% $5p^54f5d$
$5p^67s$	2S	0.5	7s01	183501.73	0.13	9% $5p^54f5d$
$5p^65f$	2F	2.5	5f02	184543.00	0.09	2% $5p^55d^2$
		3.5	5f03	184744.88	0.06	1% $5p^55d^2$
$5p^67p$	2P	0.5	7p00	198761.5	0.6	13% $5p^54f^2$
		1.5	7p01	201189.59	0.12	16% $5p^54f^2$
$5p^67d$	2D	1.5	7d01	221661.7	2.5	32% $5p^54f5d$
		2.5	7d02	222579.25	0.10	22% $5p^54f5d$
$5p^65g$	2G	3.5	5g03	226771.66	0.08	11% $5p^54f5d$
		4.5	5g04	227249.18	0.11	44% $5p^54f5d$
$5p^68d$	2D	1.5	8d01	247279.6	0.6	1% $5p^54f5d$
		2.5	8d02	247504.22	0.16	1% $5p^54f5d$
$5p^66g$	2G	3.5	6g03	248198.50	0.22	
		4.5	6g04	248211.12	0.21	
$5p^54f5d$		3.5	d301	158880.7	0.9	
		4.5	d401	161589.9	1.3	
		2.5	d202	162130.05	0.07	
		2.5	d203	163093.6	1.3	
		3.5	d302	163465.3	1.3	
		2.5	d204	163808.4	1.1	
		3.5	d303	163833.7	0.9	
		3.5	d304	165787.6	1.0	
		1.5	d103	166265.23	0.11	
		2.5	d205	167551.6	1.0	
		1.5	d104	168507.44	0.07	
		3.5	d305	169628.5	1.1	
		2.5	d206	169731.4	1.0	
		4.5	d405	170878.9	1.4	
		3.5	d306	170910.8	1.0	
		2.5	d207	171184.88	0.10	
		1.5	d105	171242.07	0.09	
		3.5	d307	171757.8	1.1	
		3.5	d308	172859.5	1.1	
		1.5	d106	172990.59	0.09	
	2.5	d208	173248.22	0.11	6% $6d$	
	4.5	d407	173302.3	1.5		
	1.5	d107	173898.10	0.10	11% $6d$	
	2.5	d209	174348.40	0.12		
	3.5	d309	175130.1	1.1		
	1.5	d108	175746.61	0.10	28% $6d$	

TABLE II. (*Continued.*)

Config.	Term	J	Desig.	Energy	Unc.	Config. int.
$5p^54f5d$		4.5	$d408$	176687.6	1.5	
		4.5	$d409$	176915.2	1.5	
		3.5	$d311$	177777.5	1.1	
		4.5	$d410$	179178.2	1.6	
		2.5	$d210$	179406.98	0.14	23% $6d$
		2.5	$d211$	180136.01	0.14	7% $6d$
		3.5	$d312$	180587.6	1.1	
		2.5	$d212$	183195.19	0.16	10% $6d$
		3.5	$d313$	183360.6	1.6	
		0.5	$d005$	183796.14	0.13	
		1.5	$d109$	184297.8	1.7	
		2.5	$d213$	185516.73	0.18	
		4.5	$d411$	186875.3	1.7	
		3.5	$d314$	187145.0	1.2	
		2.5	$d214$	187597.9	1.3	
		4.5	$d412$	188530.5	1.7	
		3.5	$d315$	189139.0	1.8	
		4.5	$d413$	191129.9	1.8	
		3.5	$d316$	191605.1	1.3	
		1.5	$d112$	191976.9	1.8	
		2.5	$d215$	192708.68	0.21	
		4.5	$d414$	193585.1	1.8	
		2.5	$d216$	194420.9	1.9	
		3.5	$d318$	195665.2	1.8	
		4.5	$d415$	196358.3	1.9	
		2.5	$d217$	196657.2	1.4	
		3.5	$d319$	197687.1	1.4	
		4.5	$d416$	197821.3	1.9	
		2.5	$d218$	197917.1	1.9	
		1.5	$d115$	200167.7	2.0	
		4.5	$d417$	200775.5	2.0	
		3.5	$d320$	201948.1	1.6	
		2.5	$d220$	203176.8	1.5	
	3.5	$d321$	203569.2	1.5		
	4.5	$d418$	208284.7	2.1		
	1.5	$d118$	210373.5	2.2		
	3.5	$d322$	223945.96	0.12	7% $5g$	
	2.5	$d222$	224055.5	2.5		
	3.5	$d323$	224919.4	1.8	6% $5g$	
	4.5	$d419$	225134.10	0.10	47% $5g$	
	1.5	$d119$	227720.9	2.6	33% $7d$	
	2.5	$d223$	229205.6	1.9	20% $7d$	
$5p^54f6s$		1.5	$s101$	196945.4	1.9	
		2.5	$s201$	199869.3	1.4	
		1.5	$s102$	201068.5	2.0	
		4.5	$s401$	202872.4	2.0	
		3.5	$s301$	204143.1	1.5	
		3.5	$s302$	204585.9	1.5	

TABLE II. (Continued.)

Config.	Term	J	Desig.	Energy	Unc.	Config. int.
		4.5	s402	204741.5	2.1	
		2.5	s202	206186.6	1.5	
		2.5	s203	207704.9	1.6	
		3.5	s303	208082.6	1.5	
		4.5	s403	211422.5	2.2	
		3.5	s304	212181.5	1.6	
		1.5	s103	213686.6	2.3	
		2.5	s204	214633.4	1.6	
		2.5	s205	227453.7	2.6	
		3.5	s305	227882.3	2.6	
		2.5	s206	230679.4	1.9	
		4.5	s404	231601.4	2.6	
		3.5	s307	232405.5	2.0	
		1.5	s104	233981.1	2.7	
		2.5	s207	234297.64	0.13	

V. THEORETICAL INTERPRETATION

A. Even-parity levels

Our interpretation of the even levels treated the one-electron configurations $5p^6nl$ together with the core-excited configurations $5p^54f5d$ and $5p^54f6s$ as a single group. Initial parameter values for $5p^54f5d$ and $5p^54f6s$ were radial integrals calculated with the Cowan code adjusted by various scale factors. Earlier studies of Ce^{2+} [19], Ce^{4+} [12], and

other lanthanides helped to determine the scale factors. For our initial calculations, the average energies of the configurations were adjusted so that the largest number of experimental levels would fit the calculated structure, taking into account observed intensities and the computed transition probabilities. Because of their large configuration-interaction (CI) integrals, three unknown core-excited configurations, $5p^54f6d$, $5p^55d6p$, and $5s5p^64f^2$, were included in the calculation, bringing the final set of basis states to $5p^6nd$ ($n=5-8$), $5p^6ns$ ($n=6,7$), $5p^6ng$ ($n=5,6$), $5p^54f5d$, $5p^54f6s$, $5p^54f6d$, $5p^55d6p$, and $5s5p^64f^2$.

One of the main difficulties in carrying out a least-square fit of the energy parameters to the observed levels for a system such as this is that the $5p^6nl$ configurations consist of only one or two levels. These are fully described by the average energy E_{av} and the spin-orbit interaction parameter ζ_{nl} . Thus, introduction of CI integrals for the one-electron configurations creates a problem of under determination of the system. Once our rough fitting was considered a good starting point for optimizing the parameters, the problem of over parametrization had to be overcome.

The 240 parameters considered included 13 configuration average energies, 40 electrostatic Slater integrals, 27 effective electrostatic parameters for far interactions with doubly excited configurations not in our basic set, 18 spin-orbit parameters, and 142 electrostatic parameters for configuration interactions. As the number of known energy levels was initially 50, a system to reduce the number of free parameters had to be adopted.

The most important reduction was accomplished by bundling the 142 CI parameters into groups that maintained their Hartree-Fock ratios throughout the calculations. The Slater parameters with the same names in the group $5p^54f5d + 5p^54f6s$ as well as the spin-orbit parameters were also varied in this way.

The effective parameters for far CI effects, which are known to improve the energies in configurations of non-

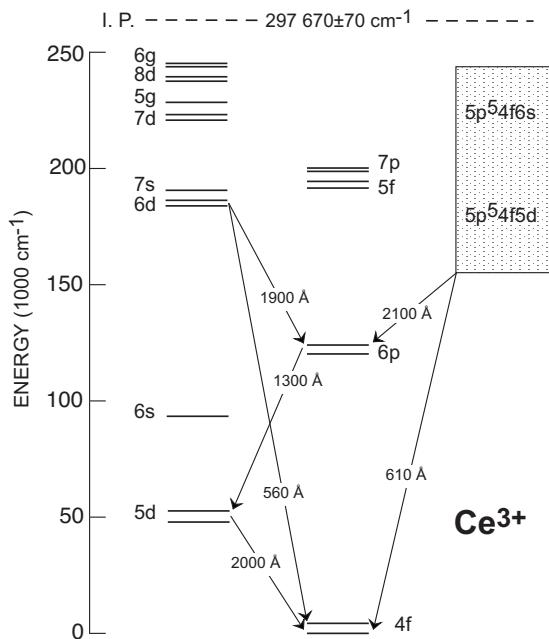


FIG. 1. Schematic transition diagram showing observed energy levels of Ce^{3+} and transitions that form the basis for accurate Ritz-type wavelengths. Wavelengths are approximate. The block for the $5p^54f5d$ and $5p^54f6s$ configurations contains about 80 energy levels.

equivalent electrons, such as $4f^N 5d$, had their initial values taken from the recent analysis of Nd^{3+} [20]. We considered the effective (nonallowed) Slater parameters $F^1(4f5d)$, $G^2(4f5d)$, and $G^4(4f5d)$, which have been successfully used in many previous studies, as well as $F^1(5p4f)$ and $F^1(5p5d)$. Since $G^2(4f5d)$ and $G^4(4f5d)$ are known to be about equal, we set $G^2(4f5d) = G^4(4f5d)$. We also arbitrarily set $F^1(5p4f) = F^1(5p5d) = F^1(4f5d)$. This reduced the 27 effective electrostatic parameters to two adjustable ones.

All parameters for the high unknown configurations were fixed at their scaled HFR values. After a few fits, predicted wavelengths and intensities were compared with the experimental spectrum. Practically, all strong lines in the 400–700 Å region with definite Ce^{3+} character could be interpreted. The location of a number of combinations with $6p$, $7p$, and $5f$ levels in the longer wavelength region 1300–3250 Å confirmed the interpretation of the upper levels.

The high-lying even levels with $J=1/2$ presented a special problem. Our calculations indicated that $7s$ should be strongly mixed with a close predicted level of $5p^5 4f 5d$. The only possibility for this level was one located 294 cm^{-1} above $7s$, 183796 cm^{-1} . However, in order to obtain convergence in the fitting process, we had to manually adjust and then fix the parameters for the $5p^6 7s$ - $5p^5 4f 5d$ interaction. Although they closely reproduce the values of the $J=1/2$ levels, the adjusted parameter values are much smaller than the HFR values. In the final parametric fit, both $J=1/2$ levels were omitted.

In the final step, 102 levels were fitted by 34 free parameters with a mean error (rms deviation) of 163 cm^{-1} . When the calculations were made without the unknown configurations $5p^5 4f 6d$, $5p^5 5d 6p$, and $5s 5p^6 4f^2$, the mean error increased to 184 cm^{-1} . In general, the agreement between the observed intensities and the transition probabilities calculated with the fitted parameters is good. Although there are some exceptions, for most of the pairs of lines connecting an upper level to the ground term, the intensities are in the same general ratio as the calculated values.

A large effect of CI is seen for the transition probabilities of the $4f$ - $5d$ resonance transitions, the strongest lines in the spectrum. These transition probabilities are reduced by a factor of nearly 2 because of interaction between $5p^6 5d$ and $5p^5 4f 5d$. A similar reduction is found in Nd^{3+} [20], Nd^{4+} [21], and Tm^{3+} [22], where the effects of $5p^6 4f^N 5d + 5p^5 4f^{N+1} 5d$ mixing on the transition probabilities of $5p^6 4f^N$ - $5p^6 4f^{N-1} 5d$ transitions have been studied.

The fitted parameter values and their standard errors are compared with HFR values in Table B, available online at EPAPS [18]. The scale factors range from 0.70 to 0.92, which is normal for these types of structures. Although the factor of 1.19 for $F^4(4f5d)$ is relatively high, similar factors are found for many fitted $F^4(fd)$ parameters throughout the periodic table.

The complete results of the least-squares fit for the even configurations, including the first three eigenvector components for each level, are given in Table C, available online at EPAPS [18]. The most important admixtures due to configuration interaction are given by total configuration percentage in Table II.

TABLE III. Measured and calculated lifetimes (ns) for the $5d$ levels of Ce^{3+} .

Level	Expt. ^{a, b}	HFR		
		This work	Zhang <i>et al.</i> ^c	Zhang <i>et al.</i> ^d
$5d_{3/2}$	$30(1^\beta + 1^\theta)$	29.3	30.5	30.3
$5d_{5/2}$	$30(1.4^\beta + 1.6^\theta)$	28.3	30.0	29.6

^aZhang *et al.* (Ref. [23]).

^b β : statistical error; θ : estimated systematic error.

^cZhang *et al.* (Ref. [23]); 12 even and 12 odd configurations.

^dZhang *et al.* (Ref. [23]); 3 odd and 2 even configurations.

B. Odd-parity levels

Our calculations for the odd configurations included the observed $5p^6 nl$ configurations as well as the unknown core-excited configurations $5p^5 4f^2$, $5p^5 5d^2$, and $5p^5 4f 6p$. The calculations show that $5p^6 4f$ and $5p^6 6p$ are not much affected by CI. However, the $5p^6 5f$ and $5p^6 7p$ configurations are surrounded by levels of $5p^5 4f^2$. Our calculations indicate that $5p^6 5f$ contains an admixture of $5p^5 4f^2$ amounting to almost 3%; for $5p^6 7p$, the admixture of $5p^5 4f^2$ is about 15%. Since the true positions of the perturbing levels of $5p^5 4f^2$ are not actually known, these admixtures cannot be calculated precisely.

In the absence of configuration interaction, all levels of $5p^5 4f^2$ are metastable and not easily detectable. Although it might be possible to locate some of them through transitions to $5p^5 4f^2$ from $5p^5 4f 5d$, the predicted transitions lie mainly at wavelengths well beyond our present observations. Therefore, we were not able to locate any levels of $5p^5 4f^2$. The higher unknown configurations $5p^5 5d^2$ and $5p^5 4f 6p$ should fall in the ranges $208\,000$ – $312\,000 \text{ cm}^{-1}$ and $228\,000$ – $275\,000 \text{ cm}^{-1}$, respectively, and interact strongly with $5p^6 6f$, which is expected to lie near $225\,000 \text{ cm}^{-1}$. We were not able to locate either of these core-excited configurations or $5p^6 6f$.

The energy parameters for the observed odd configurations are given in Table D, available online at EPAPS [18].

VI. OSCILLATOR STRENGTHS

The wave functions obtained with the fitted energy parameters were used to calculate weighted oscillator strengths gf and weighted transition probabilities gA for all classified lines. The values of $\log g_L f$, f being the oscillator strength and g_L as the statistical weight of the lower level $2J_L + 1$ are given in Table I. The values of $g_U A$, A being the transition probability and g_U as the statistical weight of the upper level $2J_U + 1$, are also given in this table.

The only measurements available for comparison with our calculated values are those of Zhang *et al.* [23]. They used time-resolved laser spectroscopy to measure lifetimes for the $5d$ levels of Ce^{3+} . The values determined with our fitted energy parameters are compared with the measured values in Table III. The agreement is remarkably good, especially since the calculated lifetimes are increased by a factor of nearly 2 due to interaction with $5p^5 4f 5d$.

Also shown in Table III are HFR lifetimes obtained by Zhang *et al.* [23] with the Cowan code using a basis set consisting of 12 odd and 12 even configurations, with no scaling of the parameters. Again, the calculated and measured lifetimes agree well. Our present results mirror the values obtained by them with a basis set limited to 3 odd and 2 even configurations and a uniform scale factor of 0.85 for the parameters (30.3 ns for $5d_{3/2}$ and 29.6 ns for $5d_{5/2}$).

VII. IONIZATION ENERGY

By using a Ritz formula to predict the binding energy of the $4f$ term, Lang [4] estimated the energy to ionize Ce^{3+} to the $5p^6\ ^1S_0$ ground level of Ce^{4+} as $296\ 197\ \text{cm}^{-1}$. No uncertainty was given. Sugar and Reader [24] revised this to $296\ 470 \pm 40\ \text{cm}^{-1}$ by finding the limit of Lang's three-member $ns(n=6-8)$ series. Since we now know that Lang's $8s$ term was spurious, the result of Sugar and Reader [24] has to be discarded.

For our present determination, we make use of the $6g$ configuration, which is the configuration least perturbed by inner-shell excitations. According to calculations with the Cowan code, the $6g$ configuration has a quantum defect of 0.0459. Isoelectronic comparisons with ions, for which an accurate ionization energy is known, indicate that this value should be corrected by a multiplicative factor of 0.98. This implies a quantum defect of 0.0450 and an effective quantum number $n^*(6g)=5.955\ 0$. The binding energy of the $6g$ configuration is thus $49\ 512\ \text{cm}^{-1}$.

According to our calculations, the $J=7/2$ and $J=9/2$ levels of $6g$ are pushed up by $39\ \text{cm}^{-1}$ and $53\ \text{cm}^{-1}$, respectively, due to perturbation by the inner-shell-excited configurations. Applying these corrections, we find the unperturbed positions for the two $6g$ levels as $248\ 159\ \text{cm}^{-1}$ ($J=7/2$) and $248\ 158\ \text{cm}^{-1}$ ($J=9/2$). This implies an average energy for $6g$ of $248\ 159\ \text{cm}^{-1}$ and an ionization energy for Ce^{3+} of $297\ 670\ \text{cm}^{-1}$.

By making calculations of the binding energy of the $6g$ configuration of Cs, Ba^+ , and La^{2+} with the Cowan code and comparing the energies with the experimental values, we estimate an uncertainty of ± 0.05 for the correction factor to the results with the Cowan code. The resulting uncertainty in the ionization energy is $38\ \text{cm}^{-1}$. We also estimate that the perturbations of $6g$ by inner-shell excitations could be uncertain by the size of the calculated perturbations or about $50\ \text{cm}^{-1}$. Combining these two uncertainties in quadrature, we obtain the final uncertainty for the ionization energy of $63\ \text{cm}^{-1}$, which we round up to $70\ \text{cm}^{-1}$.

We thus adopt the value for the ionization energy of Ce^{3+} as $297\ 670 \pm 70\ \text{cm}^{-1}$ ($36.909 \pm 0.009\ \text{eV}$).

VIII. CONCLUSION

The present work represents a study of a lanthanide ion for which transitions involving inner-shell-excited configurations account for a major part of the emission spectrum. Further in the lanthanide period, in Pr^{3+} [25], with ground configuration $5p^6 4f^2$, the mixing of $5p^6 4f 6p$ with levels of the lowest core-excited configuration $5p^5 4f^3$ has led to the identification of a few levels of $5p^5 4f^3$. In Nd^{3+} [20], with ground configuration $5p^6 4f^3$, mixing of $5p^6 4f^2 6p$ with levels of $5p^5 4f^4$ has led to the identification of some levels of $5p^5 4f^4$. However, parametric analyses for these ions were hampered by a scarcity of experimental energies. Because of the known consistency of scaling factors for the radial integrals in long sequences of elements, the present results should help to improve theoretical predictions in the spectra of more complex lanthanides.

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