PAPER

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Transition probabilities of Ce I obtained from Boltzmann analysis of visible and near-infrared emission spectra

D E Nitz[1], J J Curry[2], M Buuck[1,3], A DeMann[1,4], N Mitchell[1,5] and W Shull[1,6]

[1] Department of Physics, St. Olaf College, 1520 St. Olaf Ave., Northfield, MN 55057, United States of America
[2] National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, MD 20899, United States of America

E-mail: nitz@stolaf.edu

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Abstract

We report radiative transition probabilities for 5029 emission lines of neutral cerium within the wavelength range 417–1110 nm. Transition probabilities for only 4% of these lines have been previously measured. These results are obtained from a Boltzmann analysis of two high resolution Fourier transform emission spectra used in previous studies of cerium, obtained from the digital archives of the National Solar Observatory at Kitt Peak. The set of transition probabilities used for the Boltzmann analysis are those published by Lawler *et al* (2010 *J. Phys. B: At. Mol. Opt. Phys.* **43** 085701). Comparisons of branching ratios and transition probabilities for lines common to the two spectra provide important self-consistency checks and test for the presence of self-absorption effects. Estimated 1σ uncertainties for our transition probability results range from 10% to 18%.

Supplementary material for this article is available online

Keywords: atomic spectra, transition probability, oscillator strength, cerium

(Some figures may appear in colour only in the online journal)

1. Introduction

The radiative properties of neutral and singly ionized rare-earth atoms are required for a variety of modeling applications, especially in lighting and astrophysics research [1–3]. Some of the interest is driven by the complexity of rare-earth atomic structure and corresponding radiative spectra, the same characteristics that have stymied a complete analysis of radiative properties [4]. Neutral cerium, the subject of this work, is a typical example. The energy level analysis of Martin *et al* [5] includes more than 900 levels and his unpublished line list includes more than 20 000 classified lines. Absolute transition probabilities have been published for fewer than 20% of those lines.

The preferred method for obtaining absolute radiative transition probabilities is to combine upper level lifetimes with complete branching fractions. The former can be obtained by time-resolved laser-induced fluorescence and the latter from radiometrically calibrated emission spectra. This method can yield transition probabilities with uncertainties as low as 5%. Lawler *et al* [6] recently published transition probabilities for 2874 lines of neutral cerium using this method, on the basis of radiative lifetimes of 153 levels

[3] Present address: Department of Physics, University of Washington, Seattle, WA, United States of America.
[4] Present address: Department of Physics, Colorado State University, Fort Collins, CO 80523, United States of America.
[5] Present address: The James Franck Institute and Department of Physics, University of Chicago, 929 E 57th Street, Chicago, IL 60637, United States of America.
[6] Present address: Department of Mathematics, Emory University, 201 Dowman Drive, Atlanta, GA 30322, United States of America.

measured by Den Hartog *et al* [7]. In an earlier and less extensive study, Bisson *et al* obtained transition probabilities for 30 lines using a similar approach [8].

A complimentary technique, known as Boltzmann analysis, has been used to leverage an initial set of transition probabilities into a much larger set [9]. While this method has larger uncertainties than the lifetime/branching fraction method, it can be applied in situations where the preferred method cannot, i.e., to lines for levels whose lifetimes are unknown or whose decay patterns prevent reliable determination of branching fractions. It is well suited to providing transition probabilities for modeling applications where reasonably accurate data is needed for large numbers of lines. On the other hand, it is not the method of choice for applications requiring precise values for a small number of particular lines. Previous applications of Boltzmann analysis to neutral cerium include the work of Bisson *et al* [8], who used their determination of 30 transition probabilities from lifetime and branching fraction measurements to determine transition probabilities for an additional 228 lines, and Curry [10], who used the transition probabilities of Bisson *et al* to obtain transition probabilities for 559 lines from the intensity observations of Ce I by Meggers *et al* [11].

Here we apply the extensive set of transition probabilities obtained by Lawler *et al* [6] to carry out a Boltzmann analysis of two cerium spectra from the digital archives of the National Solar Observatory at Kitt Peak and obtain absolute transition probabilities for 5029 lines of Ce I. Of these, all but 213 are first-time measurements.

2. Boltzmann analysis

The Boltzmann analysis method has been described by Cowley [9] and Curry [10] among others. It applies when radiometrically calibrated intensities of lines emitted from a set of upper levels can be described by the expression

$$I = \beta g_u A_{ul}\, \mathrm{e}^{-E_u/kT}, \qquad (1)$$

where I is the integrated photon flux in s^{-1} for a line originating from a transition between upper level u and lower level l, A_{ul} is the absolute radiative transition probability, g_u is the upper level degeneracy $(2J_u + 1)$, E_u is the upper level energy and k is Boltzmann's constant. T, an effective temperature, and β, an intensity scale factor, are fitting parameters that depend on the spectrum. If the behavior of the emission source is consistent with equation (1), then a plot of $\ln(I/g_u A_{ul})$ versus E_u for lines whose transition probabilities are known (a 'Boltzmann plot') will produce a straight line whose slope is $-1/kT$ and intercept is $\ln(\beta)$. In practice the plot is a scatter of points and a least-squares fit, weighted to account for random uncertainties in the measured intensities and the published A_{ul} values, determines the most likely values of T and β and their uncertainties. If the Boltzmann model is found to be a satisfactory description for levels whose emission line transition probabilities are known, the assumption is made that equation (1) applies equally well for levels whose emission line transition probabilities are not known, as long as they fall within the energy range spanned in the determination of β and T. New transition probabilities for lines with known upper level energies are found by solving equation (1) using their measured intensities and the parameters β and T determined for that spectrum. Uncertainties for the new transition probabilities depend on the random uncertainties in the measured intensity I and the parameters β and T as well as deviations of upper level populations relative to the fitted model. The latter can be estimated in cases where the Boltzmann fit has high redundancy, i.e., when many lines per upper level are included in the fit.

3. The source data

The spectra used in our study were obtained from the Digital Library of the 1 m Fourier transform spectrometer of the National Solar Observatory (NSO) at Kitt Peak, Arizona [12]. Both were among the set of 14 spectra used by Lawler *et al* [6] to obtain branching fractions for 153 upper levels of Ce I. These branching fractions were combined with level lifetimes measured by the same group [7] to generate 2874 absolute transition probabilities. We use those transition probabilities in Boltzmann fits to obtain T and β for each of our chosen spectra.

3.1. EDL Spectrum acquired at Kitt Peak in 1985

Spectrum 850205R0.023 in the NSO Digital Library [12] (referred to as Spectrum 10 in Lawler *et al* [6]) was obtained in 1985 by Worden, Hubbard and Wagner and later described in detail by Bisson *et al* [8]. The source was an electrodeless discharge lamp (EDL) [13, 14] containing isotopically pure $^{140}CeI_3$ and operated at the lowest power yielding stable intensity. The spectrum covers the wavenumber range 7456–28 808 cm^{-1} and was radiometrically calibrated with a standard tungsten-strip lamp observed under identical conditions. The useful wavenumber range for obtaining reliable calibrated intensities is approximately 9000–24 000 cm^{-1}. This is the spectrum used by Bisson *et al* [8] in their determination of 258 absolute transition probabilities. Both Bisson *et al* [8] and Lawler *et al* [6] saw evidence of moderate self-absorption of the strongest lines in this spectrum. This will be discussed further in section 4.

3.2. HCL Spectrum acquired at Kitt Peak in 2002

The other spectrum from the NSO library, 020227R0.030, was obtained by Lawler in 2002 (referred to as Spectrum 1 in [6]). The source was a commercial sealed hollow cathode lamp (HCL), with a natural isotopic abundance Ce cathode and argon buffer gas, operated at 27 mA. The spectrum spans wavenumbers 7929 cm^{-1} through 34 998 cm^{-1}. The radiometric calibration generated by Lawler (and used in our study) was based on a combination of a standard tungsten-quartz-halogen lamp and the intensities of widely separated Ar I and Ar II buffer gas emission lines whose branching ratios (BRs) are well-known. This spectrum was found by

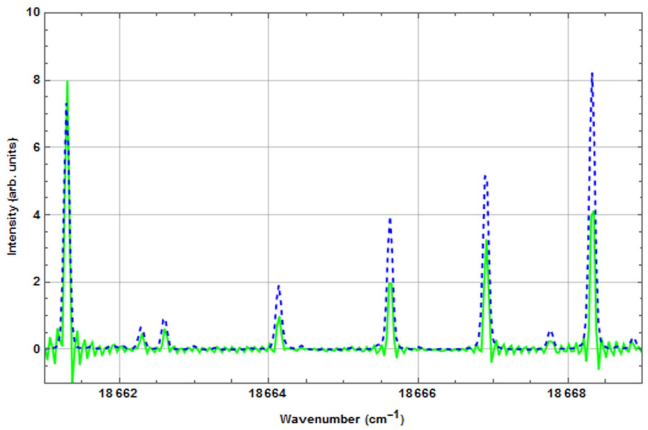

Figure 1. Samples of the cerium emission spectra used in this work (dashed/blue: EDL source; solid/green: HCL source).

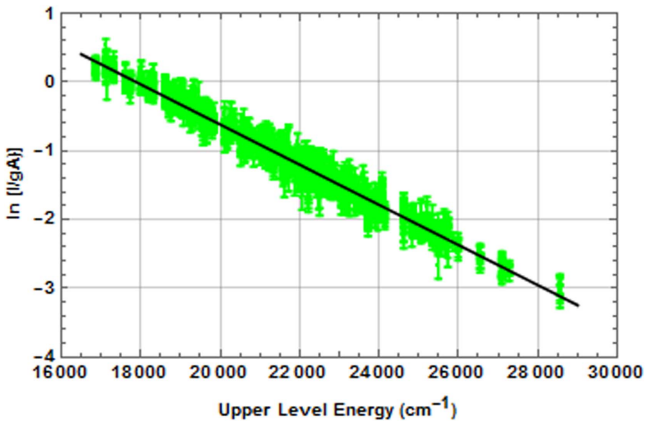

Figure 2. Boltzmann plot of the EDL spectrum using 2444 lines with absolute transition probabilities from Lawler *et al* [6]. The slope of the fitted line corresponds to a temperature of 4925 K ±14 K. The standard deviation of transition probability values from the Boltzmann fit values is 10%.

Lawler *et al* to be optically thin for even the strongest lines, making it useful in looking for evidence of self-absorption of strong lines in the EDL spectrum. This can be done on a level-by-level basis using BRs even if the spectrum cannot be described by a Boltzmann model. Somewhat to our surprise, we found that this low-current hollow cathode spectrum can in fact be described by a Boltzmann model for upper levels between 17 000 cm^{-1} and 27 000 cm^{-1}, though with significantly larger uncertainties in the Boltzmann fit parameters relative to those obtained for the EDL spectrum. It nevertheless presented the opportunity to obtain both BRs and absolute transition probabilities independent of the EDL spectrum.

4. Results

Intensities for a total of 7473 lines in the EDL spectrum and 1254 in the HCL spectrum (including the lines used for the Boltzmann analyses) were obtained by numerical integration of each line feature. We use a custom software package which searches sequentially for all dipole-allowed transitions for a given upper level and indicates the positions of all theoretically allowed transitions for neutral and singly ionized cerium and source buffer gases in the displayed wavenumber range to aid in line identification. Lines with ambiguous identification are not included. Integration limits on each side of a line are chosen individually and a fitted linear baseline is subtracted before integration. The rms noise in the fitted baseline contributes a random uncertainty to the integrated intensity for each line. In cases where overlapping lines have resolvable peaks, curve fitting with Voigt profiles is used to apportion the integrated intensity between the overlapping lines. The totals above do not include lines which were later excluded on the basis of having a linewidth significantly in excess of the average width of neighboring unblended lines or, for the EDL spectrum, intensities above a threshold at which self-absorption effects were observed.

Samples of the two source spectra are shown in figure 1 for a small spectral range centered on 18 665 cm^{-1}. The EDL spectrum is shown as a dashed curve (blue) and the HCL spectrum is shown as a solid curve (green). Each spectrum has been scaled independently. The HCL baseline shows some ringing, but this does not affect integrated line intensities. The two types of discharge yield different excited state population distributions, leading to differences in relative line intensities such as seen in the figure. For lines we observed which were present in both spectra, the signal-to-noise-ratios for the EDL spectrum were typically a factor of 8 larger than those for the HCL spectrum.

Figure 2 is a Boltzmann plot for the EDL spectrum using 2444 lines with absolute transition probabilities from Lawler *et al* [6], encompassing 135 upper levels in the range 16 870–28 560 cm^{-1}. A weighted least-squares fit gives $T = 4925$ K with a 1σ uncertainty of ±14 K, which is consistent with the value 5014 K ±111 K found by Bisson *et al* [8] for this spectrum using a much smaller set of lines and levels. This fit has a reduced χ^2 value of 0.98. When the Boltzmann fit is 'inverted,' i.e., the measured intensities are converted to transition probabilities using the Boltzmann fit parameters and compared to the original Lawler *et al* values, the standard deviation for this comparison is 10%. We interpret this standard deviation as primarily representing the deviations of level populations from a true Boltzmann distribution, since random errors associated with intensity measurements and the Lawler transition probability values should average out given that there are typically 18 lines per upper level contributing to the Boltzmann fit.

Figure 3 is a similar analysis for the HCL spectrum using absolute transition probabilities for 348 lines from Lawler *et al* including 129 upper levels in the range 17 000–27 000 cm^{-1}. Here, a weighted least-squares fit gives $T = 3733$ K ±33 K with a reduced χ^2 value of 3.61. The standard deviation between the Lawler *et al* transition probabilities and those derived from inverting the Boltzmann fit is 12%. With an average of only 3 lines per level contributing to the fit, we draw no conclusion about relative contributions of random measurement errors versus deviations from Boltzmann-like behavior in this case.

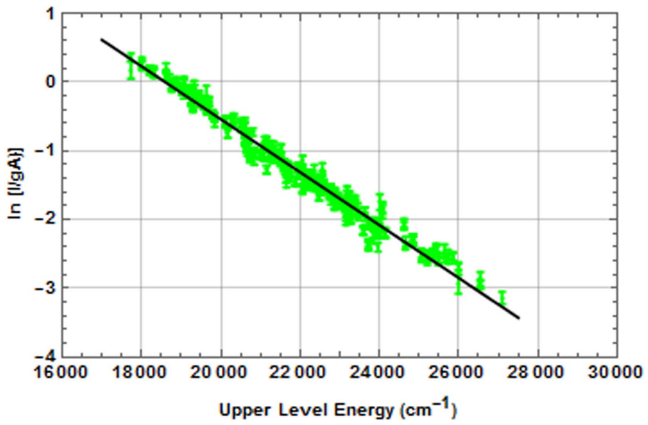

Figure 3. Boltzmann plot of the HCL spectrum using 348 lines with absolute transition probabilities from Lawler *et al* [6]. The slope of the fitted line corresponds to a temperature of 3733 K ±33 K. The standard deviation of transition probability values from the Boltzmann fit values is 12%.

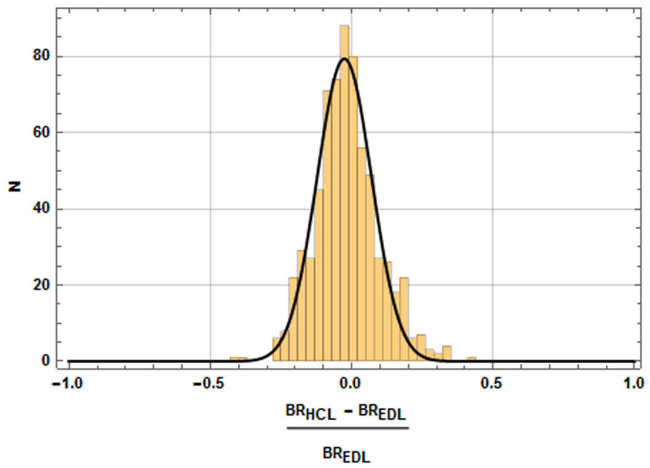

Figure 4. Histogram showing the relative difference between branching ratios for new lines common to the HCL and EDL spectra. The solid curve is a Gaussian fit to the data with a standard deviation of 10%.

Using the Boltzmann parameters from these fits, we determined transition probabilities for 5029 lines from 408 upper levels in the EDL spectrum and 906 lines from 233 levels in the HCL spectrum. All of the observed HCL lines are common to both spectra. The smaller number of lines in the HCL analysis is due to having fewer levels in the range of its Boltzmann fit and generally fewer measurable lines per level. For the EDL spectrum we were able to observe lines from all but 34 of the candidate upper levels in the range spanned by the Boltzmann analysis.

As noted earlier, both Lawler *et al* and Bisson *et al* found evidence of moderate self-absorption for some of the strongest lines in the EDL spectrum. Lawler *et al* addressed this by obtaining branching ratio measurements for the strongest lines from low current HCL spectra and using medium intensity lines as the basis to connect strong line measurements in low current spectra to weak line measurements in high current spectra. We observed evidence for self-absorption in our original Boltzmann analysis of the EDL spectrum in a plot comparing transition probabilities derived by inverting the Boltzmann fit with the Lawler *et al* input values as a function of gA. For lines with integrated intensities above 3×10^7 in the units of that spectrum, the inverted transition probabilities fell systematically lower than the input values by amounts up to 25%. We excluded these lines from our Boltzmann analysis and also used this same intensity threshold as an upper limit for EDL lines to be included in the determination of new transition probabilities.

As a further test for self-absorption effects we also compared BRs for 190 of the newly studied levels for which we were able to observe two or more lines in common between the EDL and HDL spectra. This comparison also serves as a check on the radiometric calibrations of the two spectra. We define BR = 1 for the strongest common line of each level and for the other lines we compute the ratios of their intensities to the intensity of the strongest line. To compare the BRs for the two spectra we calculate the relative difference for each line, defined as $(BR_{HCL}–BR_{EDL})/BR_{EDL}$.

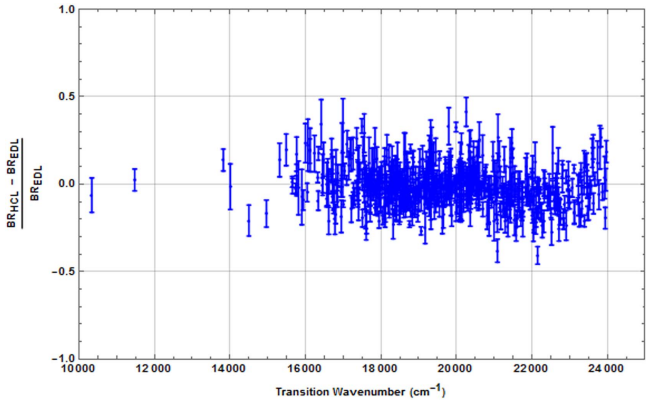

Figure 5. Relative difference between HCL and EDL branching ratios as a function of wavenumber.

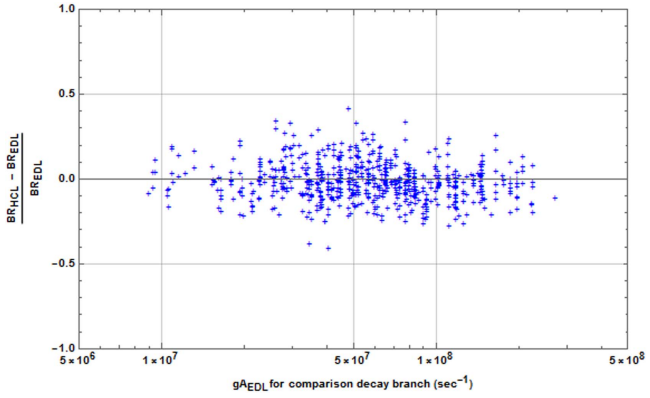

Figure 6. Relative difference between HCL and EDL branching ratios as a function of strength of the line the branch is being compared to. The error bars of figure 5 are omitted.

The results of the branching ratio comparison are shown in figures 4–7. Figure 4 is a histogram showing the distribution of the relative difference between EDL and HCL BRs for the 673 HCL lines which were not the strongest observed lines of

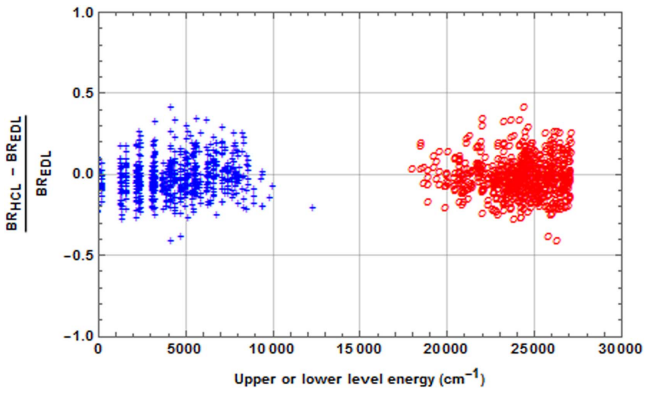

Figure 7. Relative difference between HCL and EDL branching ratios as functions of transition upper level (o/red) and lower level (+/blue). The error bars of figure 5 are omitted.

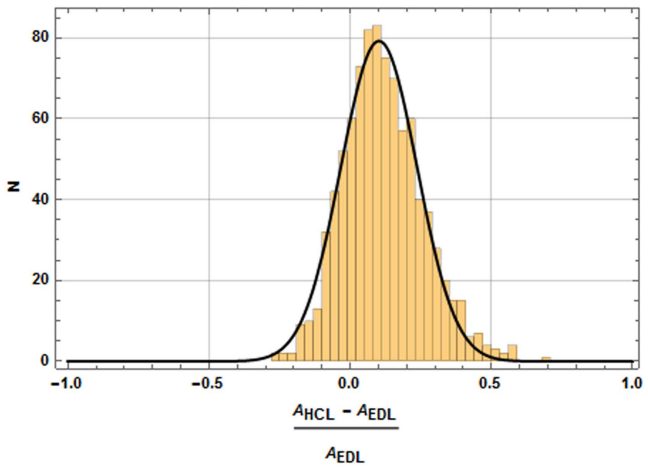

Figure 8. Histogram showing the relative difference between transition probabilities for the lines common to the HCL and EDL spectra. The solid curve is a Gaussian fit to the data with an offset of +10% and a standard deviation of 14%.

their respective upper levels. (Since the strongest common line for each level by definition has a relative difference of zero, including these in the plot would not be meaningful. Their effect is implicitly present in the sense that self-absorption of these strongest lines would show up as a shift in the distribution towards negative values of relative difference.) Overall agreement between the two sets of BRs is excellent, with a mean difference of −1.6% and a calculated standard deviation of 11%. The distribution is well-characterized by a Gaussian fit with a standard deviation of 10%.

Figures 5–7 are plots of these same branching ratio comparison data as functions of transition wavenumber, strength of the branching ratio comparison lines, and upper/lower energy level. None of these plots shows a significant systematic trend relative to the scatter in the data, which would be indicative of radiometric calibration errors or self-absorption effects. We take the overall results of figures 4–7 as evidence that self-absorption effects are not a significant factor in our analysis and that intensities have been reliably measured in both spectra. We emphasize that the branching ratio comparisons are completely independent of the Boltzmann analyses.

Figure 8 is a histogram comparing transition probabilities derived from the Boltzmann fits for the 906 lines common to the two spectra in terms of the relative difference $(A_{HCL}–A_{EDL})/A_{EDL}$. This comparison encompasses 233 (57%) of the upper levels represented in the EDL results. The HCL transition probabilities are on average about 10% higher than the EDL results and the standard deviation of the distribution is 14%. We have found empirically that the 10% offset is consistent with the mutual uncertainties of the Boltzmann fits, which are dominated by the HCL uncertainties. While inclusion of the HCL transition probabilities does not significantly improve the precision of our final results, they serve as a useful independent test of the assumption that the pattern of excited state populations determined from the Boltzmann fits can be applied to the other levels in the same range of energies.

A small fraction of our line list overlaps the previous Boltzmann analysis measurements of Bisson *et al* [8] (35 lines) and Curry [10] (178 lines). Bisson *et al*'s transition probabilities are lower than ours by a mean difference of 16% with a standard deviation of 10%. Curry's results are on average 45% higher than ours, biased by a systematic increase of deviation with decreasing line intensity. These observations are consistent with comparisons discussed previously by Lawler *et al* [6] and are not surprising given that our Boltzmann analysis employed the Lawler *et al* transition probabilities.

A table of our results listing transition probabilities, gA values and $\log(gf)$ values for 5029 lines of Ce I is available in electronic form with the online publication of this paper. A sample set of entries illustrating the format of the table is included in the appendix. Wavelengths in air were computed using energy levels from Martin *et al* [6] and the refractive index of standard air at 15 °C [15]. The last column in table indicates whether a line was observed in only the EDL spectrum or in both. For lines observed in both spectra, the transition probabilities are averages weighted by the random uncertainties of the two measurements. Uncertainties ΔA in column 9 of table, ranging from approximately 10%–18% of the A values in column 8, are 1σ estimates reflecting the random uncertainties for each line from intensity measurements and the Boltzmann fit parameters and a ±10% contribution for deviation of populations from the Boltzmann model, combined in quadrature.

5. Conclusion

We have measured transition probabilities for 5029 lines of neutral cerium between 417 and 1110 nm from a Boltzmann analysis which includes comparisons of BRs and transition probabilities in two independent high resolution Fourier transform spectra. 4816 of these are first-time measurements. This data set in combination with previously published results

increases the total number of measured Ce I transition probabilities to approximately 80% of the classified lines.

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Appendix. Data table sample

Column Headings
1-Wavelength in air (nm)
2-Upper level (1/cm)
3-Upper level parity (e = even, o = odd)
4-Upper level J
5-Lower level (1/cm)
6-Lower level parity (e = even, o = odd)
7-Lower level J
8-Transition probability A (1/s)
9-1σ uncertainty of A (1/s)
10-gA (1/s)
11-log(gf)
12-Number of spectra observed in (1 = EDL, 2 = EDL and HCL)

416.912	27 079.267	e	5	3100.151	o	4	1.90e + 5	2.30e + 4	2.09e + 6	−2.26	1
417.064	26 179.026	e	4	2208.657	o	5	2.00e + 6	2.08e + 5	1.80e + 7	−1.33	2
417.184	28 136.988	e	3	4173.494	o	4	5.61e + 5	7.21e + 4	3.93e + 6	−1.99	1
417.262	27 059.164	e	5	3100.151	o	4	1.81e + 6	1.89e + 5	1.99e + 7	−1.29	2
417.284	25 346.707	e	2	1388.941	o	3	5.73e + 5	6.29e + 4	2.87e + 6	−2.13	1
417.290	27 269.619	e	4	3312.240	o	4	9.82e + 5	1.04e + 5	8.84e + 6	−1.64	1
417.542	25 331.885	e	4	1388.941	o	3	1.07e + 6	1.11e + 5	9.59e + 6	−1.60	2

ORCID iDs

D E Nitz https://orcid.org/0000-0002-2078-2041
J J Curry https://orcid.org/0000-0003-0482-961x
A DeMann https://orcid.org/0000-0002-0127-9686
N Mitchell https://orcid.org/0000-0003-1922-8470
W Shull https://orcid.org/0000-0001-8676-8210

References

[1] Lapatovich W P 2009 *Phys. Scr.* **T134** 014024
[2] Abia C and Wallerstein G 1998 *Mon. Not. R. Astron. Soc.* **293** 89
[3] Sneden C, Cowan J J and Gallino R 2008 *Annu. Rev. Astron. Astrophys.* **46** 241
[4] Biemont E 2005 *Phys. Scr.* **T119** 55
[5] Martin W C, Zalubas R and Hagan L 1978 *Atomic Energy Levels—The Rare-Earth Elements* (*National Standard Reference Data System—National Bureau of Standards* vol 60) (Washington, DC: US Government Printing Office)
[6] Lawler J E, Chisholm J, Nitz D E, Wood M P, Sobeck J and Hartog E A D 2010 *J. Phys. B: At. Mol. Opt. Phys.* **43** 085701
[7] Hartog E A D, Buettner K P and Lawler J E 2009 *J. Phys. B: At. Mol. Opt. Phys.* **42** 085006
[8] Bisson S E, Worden E F, Conway J G, Comaskey B, Stockdale J A D and Nehring F 1991 *J. Opt. Soc. Am.* B **8** 1545
[9] Cowley C R 1983 *Mon. Not. R. Astron. Soc.* **202** 14
[10] Curry J J 2009 *J. Phys. D: Appl. Phys.* **42** 135205
[11] Meggers W F, Corliss C H and Scribner B F 1975 *Tables of Spectral Line Intensities* (*National Bureau of Standards Monograph* vol 145) (Washington, DC: US Government Printing Office)
[12] http://diglib.nso.edu
[13] Tomkins F S and Fred M 1957 *J. Opt. Soc. Am.* **47** 1087
[14] Worden E F, Gutmacher R G and Conway J G 1963 *App. Opt.* **2** 707
[15] Peck E R and Reeder K 1972 *J. Opt. Soc. Am.* **62** 958